INTERMEDIATE INORGANIC CHEMISTRY

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Intermediate Inorganic Chemistry

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PREFACE

This book is intended for the +2 Students and also for various Engineering and Medical Competitive examinations. With the introduction of the ten plus two system of education, the syllabi of our universities have undergone drastic changes. A greater emphasis is now on theoretical and conceptual approach.

This book will meet the basic requirements of the students. The subject matter has been presented in a sound logical and lucid manner. The topics have been divided into 19 Chapters. In each of them the fundamental principles have been illustrated with the help of suitable examples, diagrams, tables, data and description of experimental techniques. Recent Questions of various examinations have been given at the end of this book.

A number of problems of more general and objective types have been given at the end of each chapter.

We believe that the book will enable the students to grasp the subject rather easily and more clearly. It will help students to gain confidence in the subject.

We would gratefully welcome suggestions for the improvement of the book. All possible care has been taken to avoid any printing error, still we would be grateful if the omissions, errors and misprints detected in the book are brought to the notice of the authors.

July, 1987

Nitya Nand Sinha
Ashis Kumar Ghosh

Courses of Study of Various Examinations

Chapter	BIEC, CEE MDAT (all Bihar)	IIT	Roorkee and ISM, Dhanbad	BIT Mesra	BHU and AIIMS	WBJEE	MNREC	Central Board AISSC, AISB DSB, etc.
1. Structure of Atom	✓	✓	✓	✓	✓	✓	✓	✓
2. Radioactivity	✓	✓	✓	✓	✓	✓	✓	✓
3. Periodic Classification	✓	✓	✓	✓	✓	✓	✓	✓
4. The Chemical Bonding	✓	✓	✓	✓	✓	✓	✓	✓
5. Hydrogen, Heavy Hydrogen and Heavy Water	✓	✓	✓	✓	✓	✓	✓	✓
6. Water and Hydrogen Peroxide	×	✓	✓	×	✓	✓	✓	✓
7. Study of Carbon Group of Elements (Group IV A)	✓	✓	✓	✓	✓	✓	✓	✓
8. Study of Nitrogen Group of Elements (Group V A)	✓	✓	✓	✓	✓	✓	✓	✓
9. Study of Oxygen Group of Elements (Group VI A)	✓	✓	✓	✓	✓	✓	✓	✓
10. Study of the Elements of Halogen family (Group VII A)	✓	✓	✓	✓	✓	✓	✓	✓
11. Metals and General Metallurgical Operations	✓	✓	✓	✓	✓	✓	✓	✓
12. Compounds of Metals	✓	✓	✓	×	✓	✓	✓	×
13. Study of Sodium	✓	✓	✓	✓	✓	✓	✓	✓
14. Study of Group I B of Elements (*Cu*, *Ag*, *Au*)	✓	✓	✓	✓	✓	✓	✓	✓
15. Study of Group II A Elements	✓	✓	✓	✓	✓	✓	✓	✓
16. Study of Group II B Elements (*Zn*, *Cd*, *Hg*)	✓	✓	✓	✓	✓	✓	✓	✓
17. Aluminium (III A)	✓	✓	✓	✓	✓	✓	✓	✓
18. Tin and Lead (IV A)	×	✓	×	×	✓	×	×	×
19. Iron	✓	✓	✓	✓	✓	✓	✓	✓

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CHAPTER 1

STRUCTURE OF ATOM

1.1. Introduction

An atom is the smallest particle of a chemical element possessing the chemical properties of the element. The atoms of the different elements differ from each other in their size, mass and distribution of sub-atomic particles and chemical properties. But one thing is common to all that every atom of an element is believed to be almost spherical in shape being electrically neutral in character.

Various models regarding the structure of the atoms have been suggested. Some of these are.

(1) Thomson's atomic model, (2) Rutherford's atomic model (3) Bohr's atomic model, (4) Sommerfeld's atomic model, (5) Vector atomic model, and (6) Wave mechanical model.

The discussion of the last three are beyond the scope of this book.

1.2. Discovery of Electron : The Cathode Rays—J. J. Thomson (1897).

In 1897, Sir J. J. Thomson observed that when an electric discharge from a high potential source is passed through a gas, contained in a Geissler discharge tube (Fig. 1.1) at very low pressure (0·01 mm. *Hg*), and high voltage (10^6 V) X-rays which shot out from the cathode, is called cathode rays. On examining their properties, Thomson observed that these rays, consist of negatively charged particles.

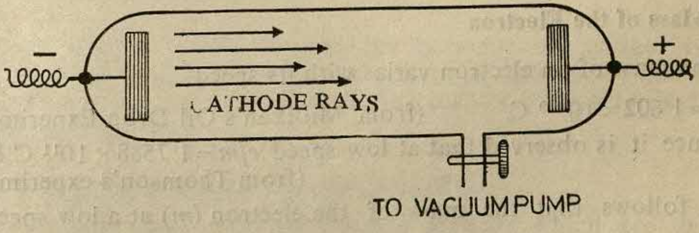


Fig. 1.1. Production of Cathode rays

Properties of Cathode rays—1. Cathode rays are shot out normally from the surface of the cathode irrespective of the position of anode.

2. Cathode rays are found to be made up of *fast moving electron* therefore they are negatively charged.

3. Cathode rays travel in straight lines in the free space with high speeds varying from 10^7 to 10^8 ms^{-1}.

4. They exert mechanical pressure by virtue of their momentums.

5. Cathode rays produce enough heat when they are allowed to fall on matter (by virtue of Kinetic Energy).

6. They ionise a gas through which they pass and make it conducting.

7. Cathode rays exhibit fluorescence and the glow colour is different for different substances (e.g. Willemite green, strontianite blue)

8. Cathode rays are deflected by magnetic and electric fields. The direction of their deflection in magnetic and electric field confirms that they carry negative charge.

9. They affect a photographic plate, similar to that of light.

10. When cathode rays are stopped by a heavy metal target (*W*,*Pt*,*Mo*) a penetrating radiation is emittted, which is known as *X*-rays.

However, it was observed that the electrons have the same properties (irrespective of any gas or material used for electrode). This clearly indicates that electrons are common constituents of all matter. Thomson further confirmed this experimentally by determining the $\frac{\text{charge}}{\text{mass}}$ (e/m) ratio (specific charge for the electron) and found it to be almost constant. Hence, electron is one of the *fundamental particle*.

1.3. Mass of the Electron

The mass of an electron varies with its speed.

$e = 1{\cdot}602 \times 10^{-19}$ C. (from Millikan's Oil Drop Experiment)

Since it is observed that at low speed $e/m = 1{\cdot}7588 \times 10^{11}$ C kg^{-1} (from Thomson's experiment)

It follows that the mass of the electron (m) at a low speed is given by

$$m = \frac{e}{e/m} = \frac{1{\cdot}6020 \times 10^{-19} C}{1{\cdot}7588 \times 10^{11} \text{ C/kg}} = 9{\cdot}1091 \times 10^{-31} \text{ kg}$$

This is called *rest mass of electron.*

The average mass of hydrogen atom (m_H) is given by

$$m_H = \frac{\text{Atomic weight of hydrogen}}{\text{Avogadro's number}} = \frac{1{\cdot}008}{6{\cdot}023 \times 10^{23}}$$

$$= 1{\cdot}6738 \times 10^{-24} \text{ g.}$$

$$\therefore \quad m_H = 1{\cdot}6738 \times 10^{-27} \text{ kg.}$$

$$m_e = \text{mass of electron} = 9{\cdot}1091 \times 10^{-31} \text{ kg}$$

$$\text{or,} \quad \frac{m_H}{m_e} = \frac{1{\cdot}6738 \times 10^{-27} \text{ kg}}{9{\cdot}1091 \times 10^{-31} \text{ kg}} = 1837$$

Therefore, average mass of hydrogen atom is 1837 times greater than the mass of electron.

$$\text{or, the mass of electron on the atomic mass scale} = \frac{1{\cdot}008}{1837}$$

$$= \mathbf{0{\cdot}0005487 \text{ amu.}}$$

1.4. Discovery of Proton. The Positive Rays;

Since atoms are known to be electrically neutral and the mass of even the lightest atom i.e., hydrogen atom is about 1837 that of electron. It is obvious that an equal magnitude of positive electricity must also be present in an atom.

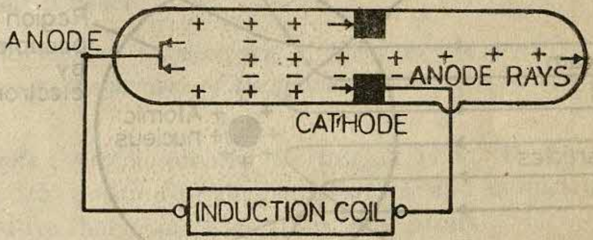


Fig. 1.2. Discharge tube for studying positive particles

E. Goldstein (1886) showed the presence of another type of radiation that passed through the holes in the cathode and carried positive charge. These rays are called **positive rays** or **anode rays** or **canal rays** (fig. 1.2).

1.5. Properties of Pasitive/Anode/Canal/Rays.

1. They possess positively charged particles which are deflected by electric and magnetic field. But the direction of deflection is opposite to that of cathode rays, showing that these particles possess positive charge.

2. Their charge (*e*) and mass (*m*) are found to depend on the nature of the gas in the discharge tube.

3. They travel in straight line.

4. They can penetrate through small thickness of metal foils.

5. They can produce ionization in gases.

6. These particles contain unit positive charge which are later known as protons. Hence proton is also an another universal constituent of all atoms.

1.6. The Nuclear Model, Existence of Nucleus, α-ray Scattering Experiment, Rutherford's Model (1911).

Experiment : Rutherford (1911) bombarded a thin sheet of gold foil (0·004 mm) with fast moving particles (i.e., Helium particles) obtained from a radioactive source (from Po, Rn). He observed that most of the particles passed through the atoms without suffering any deflection. Some were deflected from their straight path while one in 20,000 were deflected through 90° or even wider angles (fig. 1.3).

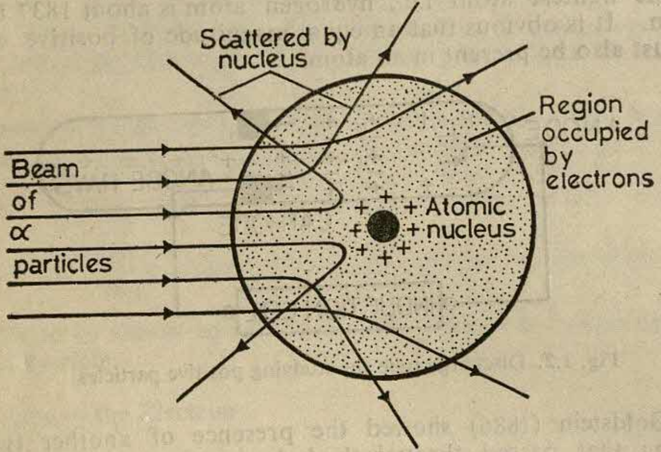


Fig. 1.3. Scattering of α-particles on their interaction with the nuclei of atom in a metallic foil.

Observation : (1) The most of the space inside an atom is *empty*.

2. The central part of the atom, known as nucleus contains whole of the *positive charge* of the atom and nearly whole of the mass (Nucleus contains protons).

3. The size of the atom is in the order of 10^{-8} cm. (10^{-10} m) and the size of the nucleus is in the order of 10^{-12} cm to 10^{-13} cm (10^{-14} m to 10^{-15} m) or 1 fermi. (1 fermi $= 10^{-15}$ metre)

4. Electrons are not stationary but are moving round the nucleus in circular orbits like the solar system.

1.7. Defects of Rutherford's Model :

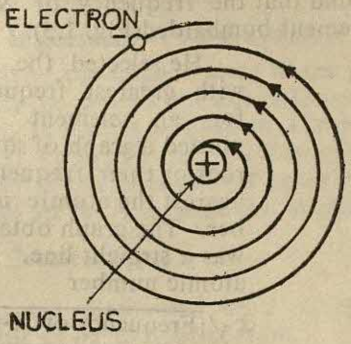


Fig. 1.4.

1. It contradicted electrodynamic theory. According to this theory, the negatively charged revolving electrons loose energy and its orbits become smaller. Therefore, electrons will fall into the nucleus, thereby making the atom unstable. (Fig. 1.4)

2. According to this model, the number of electrons in different orbits are not fixed.

3. Rutherford model could not explain the spectral lines of hydrogen atom.

1.8. Atomic Number

Atomic number is numerically equal to the positive charge on the nucleus or the number of the planetary electrons in case of neutral atom.

Example : Atomic number of oxygen is 8. It means that it occupies 8th position in the periodic table and its nucleus contains eight positive charge and 8 electrons in its orbits.

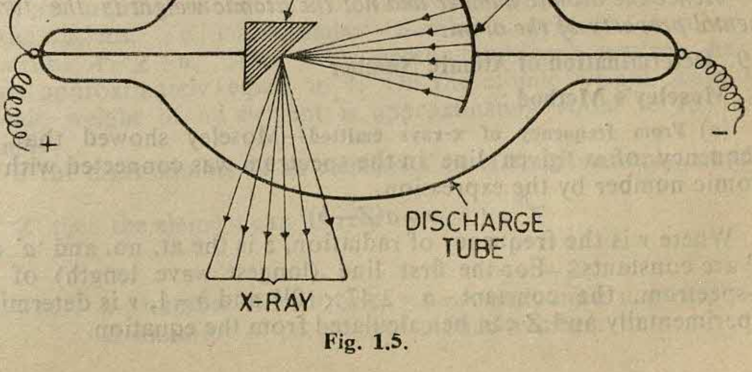


Fig. 1.5.

Moseley, an English physicist, in 1913 developed a highly ingenius method of determining atomic number which is based on the measurement of X-ray spectra of the elements. He bombarded different elements with cathode rays and found that the frequency of X-ray emitted was characteristic of the element bombarded(Fig. 1.5).

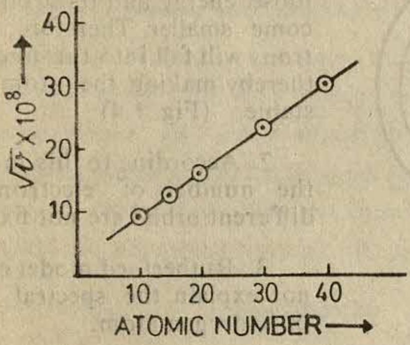


Fig. 1.6

He selected the rays with greatest frequency for an element and plotted a graph of square root of their frequencies against the atomic number. The graph obtained was a straight line. i.e., atomic number $\propto\sqrt{(\text{Frequency of X-rays})}$ (Moseley's law). Since X-rays frequency of an element depends on the internal structure of the atom, the atomic number should be a fundamental characteristics of the atom. But when the same frequencies are plotted against atomic weights, no such relationship is obtained.

Now since the frequency of X-ray emitted by each element depends on the internal structure of the atom and consequently the atomic number, the latter must be an important characteristic property of the atom. The fact that no two elements can have the same atomic number though they have that same at atomic weight (Isobars).

Potassium—At. no. = 19 At. wt. = 40
Calcium —At. no. = 20 At. wt. = 40

More over an element can have different atomic weight but can have only one atomic number (Isotopes).

Hydrogen : At. No. = 1 but At. wts. = 1, 2, 3

Hence the atomic number and not the atomic weight is the fundamental property of the atom.

1.9. Determination of Atomic Number

Moseley's Method :

(a) **From frequency of x-rays emitted**—Moseley showed that the frequency of a given line in the spectrum was connected with the atomic number by the expression.

$$\nu = a(Z-b)^2$$

Where ν is the frequency of radiation, z is the at. no. and 'a' and 'b' are constants. For the first line (longest wave length) of the K-spectrum, the constant, $a = 2{\cdot}47\times10^{15}$ and $b = 1$, ν is determined experimentally and Z can be calculated from the equation.

(b) **From scattering of α-particles**—Sincc atomic number is equal to the net positive charge on the nucleus, it can be determined by measuring the scattering of α-particles produced by bombardment to thin sheets of elements.

1.10. Importance of atomic number

(i) In the improvement of the periodic table.
(ii) To explain the anomalous pairs between Argon and potassium, Tellurium and Iodine, Cobalt and Nickel.
(iii) To explain the position of isotopes.
(iv) In the discovery of new element in the periodic table.
(v) In the determination of structure of atom.

1.11. Neutron $\left({}_0^1n\right)$

It was discovered by J. Chadwick in 1932 by bombardment of α-particles on Beryllium atom.

$$\underset{\text{Beryllium}}{{}_4^9Be}+\underset{\alpha\text{-particles}}{{}_2^4He}={}_0^1n+{}_6^{12}C$$

or it may be written as ${}^9Be\ (\alpha, n)$

Its absolute and relative charge is zero. Its absolute mass in gram is $1{\cdot}66702\times10^{-24}$ gm or $1{\cdot}66702\times10^{-27}$ kg but its relative mass is one. It is also one of the fundamenal particle present in the nucleus of all atoms except hydrogen. It takes part in nuclear reactions. The number of neutrons can be calculated as follows,

$$\boxed{n=A-Z}$$

Where n = number of neutrons,
A = Mass number or atomic mass or number of nucleons
Z = Atomic Number.

Atomic number is the number of protons or number of electrons for neutral atoms.

1.12. Atomic Mass : (Mass Numbers)

Mass number is the sum of number of protons and neutrons in the nucleus. i.e., mass number = number of protons + number of neutrons $A=Z+n$. Since each proton and each neutron has a mass approximately equal to 1. On the atomic weight scale, the **atomic weight** of an element is approximately equal to its mass number.

If the mass number of an element X be A and its atomic number be 'Z' then the element can be represented by $\overset{A}{\underset{Z}{X}}$

$$n=A-Z$$

where n = number of neutrons, A = Atomic mass number,
Z = number of protons, or atomic number.

TABLE

Main Elementary Particles

Particle	*Classical radius in metre*	*Charge in Coulo mb (e)*	*. Nature of charge*	*Rest mass in kg*	*specific charge (e/m) coulomb/kg*	*Discovered by*	*year of discovery*	*Nature of stability in the free state*
Electron (*e*)	$2{\cdot}82\times10^{-15}$	$1{\cdot}6\times10^{-19}$ Relative -1	Negative	$9{\cdot}11\times10^{-31}$ Relative 1/1837 unit	$1{\cdot}76\times10^{11}$	J. J. Thomson	1897	stable
Proton (*p*)	$1{\cdot}20\times10^{-15}$	$1{\cdot}6\times10^{-19}$ Relative $+1$	Positive	$1{\cdot}672\times10^{-27}$ Relative 1 unit	$9{\cdot}56\times10^{7}$	E. Goldstein	1915	stable
Neutron (*n*)	$1{\cdot}20\times10^{-15}$	zero	Neutral	$1{\cdot}674\times10^{-27}$ Relative 1 unit	zero	J. Chadwick	1932	unstable in free state (Mean life is equal to 12·8 minute.

Some Unstable Particles

Positron $(+{}^{0}_{1}e$ or $\beta^{+})$

Anderson discovered a new fundamental particle named positron during study of cosmic rays. It has negligible mass and same charge as the electron. But in this case, the charge is positive and hence named as positron. They have a short life (about 10^{-8} sec.) and unite with electrons to form electro-magnetic radiation.

1.13. Meson

In 1935 Yukawa reported the existence of another particle with mass in between that of proton and electron in cosmic rays. It was named meson. The charge may be positive, negative or zero.

1.14. Neutrino (ν)

In 1927, Pauli, suggested the existance of a particle named neutrino possessing a variable mass less than that of an electron. The charge on this particle is zero. Allen and Rodebeck, 1952, showed their free existence.

1.15. Antiproton (p^-)

In 1955, Segre revealed the existence of another new particle with a mass equal to that of a proton but with negative charge. It was named antiproton. Such a particle could not be expected to exist free in nature.

Particles Constituting The Atom

TABLE

Name	*Symbol*	*Discoverer*	*Charge (Relative)*	*Mass (At Rest)*
Electron	$^{0}_{-1}e$	J. J. Thomson	−1	1/1837 of *H*-atom
Positron	$^{0}_{+1}e$	C. D. Anderson	+1	1/1837 of *H*-atom
Neutron	$^{0}_{1}n$	J. Chadwick	0	1·0089
Proton	$^{1}_{1}H$	E. Goldstein	+1	1·0081
Neutrino	ν	W. Pauli	0	1·0089
Antiproton	p^-	Segre	−1	1·0081
Meson	μ	H. Yukawa	+1, −1, Zero	0·115

16.4. Neils Bohr's Model, Theory of Stationary Orbit (Hydrogen Spectrum, Circular Orbit) (One Electron System) Like (H, He^+ Li^{2+}). Neils Bohr (1913) pointed out that Rutherford model of the atom is defective and represents an unstable atom because electrons due to the loss of energy would gradually shorten their orbits and finally fall into the nucleus. This defect was overcome with the help of quantum theory. He made the following postulates.

1. The electrons are moving in certain fixed or stationary orbits. The angular momentum of electron of mass 'm' moving in a circular orbit of radius 'r' and at a constant velocity v is given by mvr which is an integral multiple of $\frac{h}{2\pi}$ i.e., $mvr=\frac{nh}{2\pi}$ where 'n' is the number of orbits.

2. An electron moving in a particular energy level is associated with a definite energy and does not lose it so long as it moves in that orbit i.e., the electrons while revolving in these orbits do not emit or absorb radiations.

3. Energy is emitted or absorbed only when an electron jumps from one orbit to another. There is radiation (emission, loss) of energy when they jump from outer to inner orbit (higher to lower energy level, L to K-orbit) but reverse will be the case in absorption.

$$\triangle E=E_2-E_1=hv=\frac{hc}{\lambda}$$

Where h = planck's constant, $v(nu)$ = The frequency of radiation absorbed or emitted, c = Velocity of light.

4. The electrons move round the nucleus in circular orbits

1.17. Bohr's Theory of Hydrogen Atom

By applying the concept of quantisation of energy and the laws of classical mechanics, Bohr in 1913 worked out a number of mathematical expressions such as those of radius of nth orbit, energy of an electron in the nth orbit etc. These expressions gave a satisfactory explanation for the hydrogen spectrum etc.

1. Radius of the *n*th orbit (r_n)—Consider an electron revolving round the nucleus in first stationary orbit.

Let, m = mass of electron; e = charge on electron
r = radius of the orbit; v = the tangential velocity.

Evidently on the revolving electron two types of forces are acting (i) *centrifugal force* which is due to the motion of the electron and tends to take the electron away from its orbit. It is equal to $\frac{mv^2}{r}$ and acts outwards from the nucleus. (ii) *Centripetal force* (also called electrostatic force of attraction) which exists between the revolving electron and the nucleus and tends to pull the electron towards the nucleus. It is given by Coulomb's inverse square law and is, therefore, equal to $-Ze\times e/r^2=-\frac{Ze^2}{r^2}$. It acts towards the nucleus.

In order that the electron may keep on revolving in its orbit, these two forces, which act in opposite directions must balance each other i.e.

$$\frac{Ze^2}{r^2}=\frac{mv^2}{r} \text{ or } v^2=\frac{Ze^2}{mr}. \quad \text{.. (i)}$$

From the principle of quantisation as applied to the revolving electron, we know that

$$mvr=\frac{nh}{2\pi} \text{ or } v^2=\frac{n^2h^2}{4\pi^2mZr^2}.$$

Putting this value in equation (i) we have

$$\frac{Ze^2}{mr}=\frac{n^2h^2}{4\pi^2m^2r^2} \text{ or } r=\frac{n^2h^2}{4\pi^2mZe^2} \quad \text{.. (ii)}$$

where r_n = radius of the nth orbit.

or

$$\boxed{r_n=\frac{Zn^2h^2}{4\pi^2mZe^2}}$$

In *SI* unit the value of r_n is given by multiplying the r_n by $4\pi\epsilon_0$

$$\therefore \quad r_n=\left(\frac{\epsilon_0h^2}{\pi mZe^2}\right)n^2$$

where ϵ_0 is the permitivity of the free space $\frac{1}{4\pi\epsilon_0}=9\times10^9\text{Nm}^2\text{c}^{-2}$

Since all the terms on the right hand side of the above equation, except n, are fixed, radius of the nth orbit is proportional to n^2 (i.e. $r_n \propto n^2$)

On putting $n=1$ in the above expression of r_n we get the radius of the first orbit of hydrogen atom which is represented as r_1, r_H or a_0 and is called **Bohr radius.** Thus

$$\boxed{r_1(r_H \text{ or } a_o)=\frac{h^2}{4\pi^2mZ^2e}}$$

On putting $h=6{\cdot}6256\times10^{-34}$ Js
$Z=1$ for hydrogen

$\pi=3{\cdot}14$; $m=9{\cdot}109\times10^{-31}$ kg
$e=1{\cdot}602\times10^{-19}$ coulomb.

in the above expression for r_1 we get the value of r_1 as :

$$r_1=\frac{(6{\cdot}6256\times10^{-34})^2}{4\times(3{\cdot}14)^2\times(9{\cdot}109\times10^{-13})\times(1{\cdot}602\times10^{-19}}$$

or

$$\boxed{r_1(r_H \text{ or } a_0)=0{\cdot}53\times10^{-10}\text{m}=0{\cdot}53\text{Å}}$$

Relation Between r_n and r_1 : On dividing the equations giving the values of r_n and r_1, we get

$$\frac{r_n}{r_1}=\frac{n^2h^2}{4\pi^2mZe^2}\times\frac{4\pi^2mZe^2}{h^2}=n^2$$

$$\text{or,}\quad \boxed{r_n=r_1\times n^2=0{\cdot}53\times n^2\,\text{Å}}$$

Thus the values of $r_2, r_3\ldots$.(in Å) in terms of r_1 are given as

$$r_2=0{\cdot}53\times2^2=2{\cdot}12\text{Å};\quad r_3=0{\cdot}53\times3^2=4{\cdot}77\text{Å}\ldots.$$

2. Energy of the electron in *n*th orbit (E_n)—Energy (E_n) of an electron moving in the *n*th orbit is the sum of its kinetic energy (K. E.) and potential energy (P. E.). K. E. which is due to the motion of the electron is equal to $\frac{mv^2}{2}$ and P.E. which is because of the fact that the electron lies in the field of the positive nucleus is equal to $-e^2/r$.

Thus $$E_n=\frac{1}{2}mv^2-\frac{Ze^2}{r}\qquad\text{.. (ii)}$$

Again we know that in order to keep the electron revolving in its orbit the centrifugal force $\left(=+\frac{mv^2}{r}\right)$ and the centripetal force $\left(=-\frac{Ze^2}{r^2}\right)$ acting on the revolving electron must balance each other, i. e. $\frac{Ze^2}{r^2}=\frac{mv^2}{r}$ or $mv^2=\frac{Ze^2}{r}$. On putting mv^2 equal to $\frac{Ze^2}{r}$ in the expression (ii), we get

$$E_n=\frac{Ze^2}{2r}-\frac{Ze^2}{r}=-\frac{Ze^2}{2r}.\qquad\text{.. (iii)}$$

Now, we know that, $r=\frac{n^2h^2}{4\pi^2mZe^2}$ in the equation (iii) we get

$$E_n=-\frac{e^2}{2}\times\frac{4\pi^2mZe^2}{n^2h^2}$$

$$\text{or}\quad\boxed{E_n=-\frac{2\pi^2mZe^4}{n^2h^2}}$$

In *SI* unit the energies E_n are given by dividing by $(4\pi\epsilon_0)^2$

$$E_n = -\frac{mZ^2e^4}{8\epsilon_0^2 n^2 h^2}$$

The negative sign occuring in the above equation implies that $E_n \alpha n^2$. Thus if the energies associated with 1st, 2nd, 3rd,....nth orbits are $E_1, E_2, E_3 \ldots \; E_n$, these will be in the order.

$$E_1 < E_2 < E_3 < \ldots . E_n$$

Energy (E_1) of the electron moving in the 1st Bohr orbit is obtained by putting $n=1$, in the energy expression of E_n. Thus

$$\boxed{E_1 = -\frac{2\pi^2 mZe^4}{h^2}}$$

Putting the values of π, m, e, Z and h in the above expression of E_1 we get the numerical value of E_1 as

$$E_1 = \frac{2\times(3\cdot14)^2\times(9\cdot109\times10^{-31})1\cdot602\times10^{-19}}{(6\cdot6256\times10^{-34})^2}$$

$$= -21\cdot79\times10^{-19} \text{ ergs/atom} = -13\cdot6 \text{ eV/atom.}$$
$$= -313\cdot6 \text{ k cal/mole.}$$

(Note that 1 erg $=6\cdot2419\times10^{11}$ *eV*; 1 *eV* $=23\cdot06$ kcal)

Relation between E_n and E_1 Evidently.

$$\frac{E_n}{E_1} = \frac{2\pi^2 mZe^4}{n^2h^2} \times \frac{h^2}{2\pi^2 mZe^4}$$

Or, $$\boxed{E_n = E_1 \times \frac{1}{n^2} = -\frac{13{\cdot}6}{n^2}\; eV/\text{atom} = -313\cdot6 \text{ k cal/mole.}}$$

Thus the values of E_2, E_3, E_4 etc. (in *eV*) in terms of E_1 are given by

$$E_2 = -\frac{13\cdot6}{2^2} = -3\cdot4\; eV/\text{atom}$$

$$E_3 = -\frac{13\cdot6}{3^2} = -1\cdot51\; eV/\text{atom}$$

$$E_4 = -\frac{13\cdot6}{4^2} = -0\cdot85\; eV/\text{atom.}$$

3. Frequency (ν), wave number ($\bar{\nu}$) and Wave length (λ) of the spectral lines of hydrogen atom.

(i) $\nu = \dfrac{2\pi^2 e^4 Zm}{h^3}\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$

(ii) $\bar{\nu} = \dfrac{1}{\lambda} = \dfrac{2\pi^2 e^4 Zm}{h^3 c}\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)\left(\text{Since } \bar{\nu} = \dfrac{1}{\lambda}\right).$

In SI unit the value of $\bar{\nu}$ is given by dividing $(4\pi_0\epsilon)^2$

$$\bar{\nu} = \frac{1}{2} = \frac{mZ^2e^4}{8\epsilon_0^2\, ch^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

(iii) $\bar{\nu} = \dfrac{1}{\lambda} = R_H\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$

Where R_H = Rydberg's constant $= 2\pi^2 e^4 m/h^3 c$.

Its calculated value (R_H) is equal to 109,679 cm^{-1}.

or $1{\cdot}09679 \times 10^7 m^{-1}$

In $SI\ R_H = mZ^2e^4/8\epsilon_0^2 ch^3$

The above equation thus reduces to

$$\boxed{\bar{\nu} = \frac{1}{\lambda} = 109{,}679\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\text{cm}^{-1}}$$

With the help of equation (i) and (ii) we can calculate the frequency (ν), wave number ($\bar{\nu}$) and wavelength (λ) respectively of the lines observed in the hydrogen spectrum provided that we know the values of n_1 and n_2. The values of n_1 and n_2 are fixed from the electronic transitions.

In SI, unit, by dividing $4\pi\epsilon_0$, $V_n = \dfrac{Ze^2}{2\epsilon_0 nh}$

4. Velocity of electron in the *n*th orbit :

We know that (From equation-(i)—

$$mv_n^2 = \frac{Ze^2}{rn};\quad mv_n r_n = \frac{nh}{2\pi}$$

$$\frac{mv_n^2}{mv_n r_n} = \frac{Ze^2}{r_n} \times \frac{2\pi}{nh} \quad \text{or,} \quad v_n = \frac{2\pi Ze^2}{nh}$$

Thus the velocity of electron is seen to decrease with increase in quantum number. In other words electron moves with lower speed in higher orbit and vice versa.

1.18. Electronic Transition and Origin of the Spectral Lines of Hydrogen Atom :

Although hydrogen atom contains only one electron, its spectrum gives a large number of lines. This is because any given sample of hydrogen contains almost infinite number of atoms. Under the normal conditions the electron of each hydrogen atom remains in the ground state near the nucleus i.e. in the energy level with $n=1$ (K-shell). There are several fixed energy states in hydrogen atom (or any atom in general) when electronic transition from higher energy states to lower ones take place in excited hydrogen atoms, five well-defined spectral series of lines due to emission of photons occur. This is shown in the diagram below —

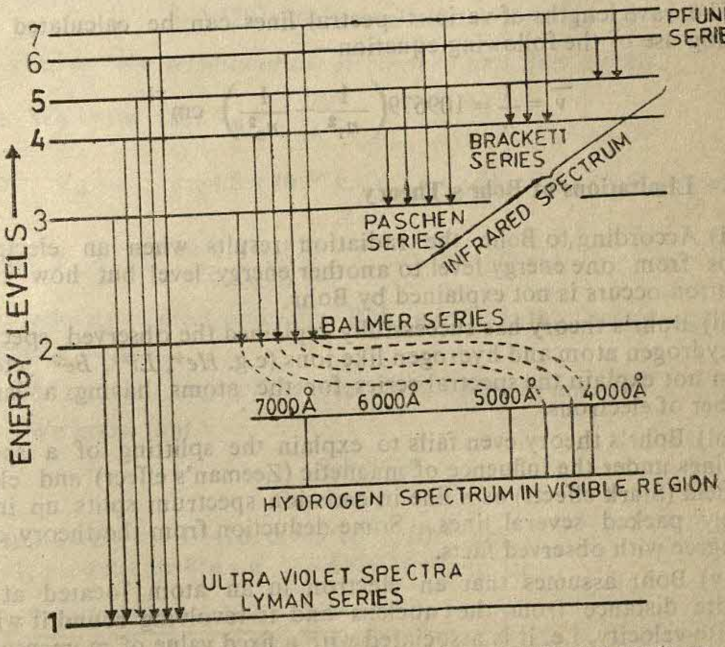


Fig. 1.7. Energy level diagram for the observed hydrogen spectrum.

Electronic transitions and values of n_1 and n_2 for various spectral series of hydrogen spectrum.

TABLE

Series of lines	*Electron jumps to an energy level with n_1=* 1,2,3,4,5,......	*Electron jumps to an energy level with n_2=* $(n_1+1), (n_1+2)$	*Spectral region*	*Wavelength*
1. Lyman series.	1	2, 3, 4,....etc.	Ultraviolet	Less than 4000 Å
2. Balmer series.	2	3, 4, 5,....etc.	Visible	Between 4000Å to 7000Å
3. Paschen series.	3	4, 5, 6,...etc.	Near infrared	More than 7000 Å
4. Brackett series.	4	5, 6, 7,...etc.	Far infrared	More than 7000 Å
5. Pfund series.	5	6, 7, 8,...etc.	Far infrared	More than 7000 Å

The wave lengths of various spectral lines can be calculated by making use of the following equation—

$$\bar{\nu} = \frac{1}{\lambda} = 109679\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{cm}^{-1}$$

1.19. Limitations of Bohr's Theory

(i) According to Bohr, the radiation results when an electron jumps from one energy level to another energy level but how this radiation occurs is not explained by Bohr.

(ii) Bohr's theory has successfully explained the observed spectra for hydrogen atom and hydrogen like ions (e.g. He^+, Li^{2+}, Be^{3+} etc.), it can not explain the spectral series for the atoms having a large number of electrons.

(iii) Bohr's theory even fails to explain the splitting of a spectral lines under the influence of magnetic (Zeeman's effect) and electric field (Stark effects) as a line in emission spectrum splits up into closely packed several lines. Some deduction from the theory did not agree with observed facts.

(iv) Bohr assumes that an electron in an atom located at a definite distance from the nucleus and is revolving round it with definite velocity, i.e. it is associated with a fixed value of momentum. This is against the **Heisenbergs Uncertainty Principle.**

(v) Bohr's theory cannot explain the stark effect,

(vi) There was no satisfactory justification for the assumption that the electron can rotate only in those orbits in which the angular momentum of the electron (*m*, *v*, *r*) is a whole number multiple of $h/2\pi$ i. e. he could not give any explaination for using the principle of *quantisation of angular momentum* and it was introduced by him arbitrarily.

SOLVED PROBLEMS

1. *Find out the radius of the first Bohr's orbit of hydrogen.* ($h=6{\cdot}6\times10^{-27}$ *erg sec.*) **[I S M 1985]**

Sol. We know that

$$r=\frac{n^2h^2}{4\pi^2mZe^2} \text{ where } n=1;\ Z=1 \text{ for hydrogen atom}$$

mass of electron $(m)=9{\cdot}1\times10^{-28}$ gm; $e=4{\cdot}8\times10^{-10}$ e.s.u.

$$r=\frac{1^2\times(6{\cdot}6\times10^{-27})^2}{4\times(3{\cdot}14)^2\times9{\cdot}1\times10^{-28}\times(4{\cdot}8\times10^{-10})^2}$$

$$=0{\cdot}529\times10^{-8}\text{ cm}=0{\cdot}529\ \text{Å}\ [\text{as } 1\ \text{Å}=10^{-8}\text{ cm}]$$

2. *Find out the velocity of the electron in first Bohr's orbit.*

Sol. We know that $V_n=\dfrac{2\pi Ze^2}{nh}$

Now $V_n=V_1$; $e=4{\cdot}8\times10^{-10}$ e.s.u.; $n=1$; $h=6{\cdot}6\times10^{-27}$ erg sec. $Z=1$

Then $V_1=\dfrac{2\times3{\cdot}14\times(4{\cdot}8\times10^{-10})^2}{1\times6{\cdot}6\times10^{-27}}=2{\cdot}82\times10^8$ cm/sec.

The velocity of electron in first Bohr's orbit is thus nearly $\frac{1}{187}$ of the velocity of light.

3. *Find out the energy of the electron in hydrogen atom.*

Sol. We know that :

$$E_n=\frac{2\pi^2mZ^2e^4}{n^2h^2}$$

Here $E_n=E_1$, $\pi=3{\cdot}1416$, $m=9{\cdot}109\times10^{-28}$ gm
$Z=1$, $e=4{\cdot}8\times10^{-10}$ e.s.u., $h=6{\cdot}6\times10^{-27}$ erg sec

$$E_1=\frac{2\times(3{\cdot}1416)^2\times9{\cdot}109\times10^{-28}\times(4{\cdot}8\times10^{-10})^4}{1\times1\times(6{\cdot}6\times10^{-27})^2}=$$

$$=-21{\cdot}76\times10^{-12}\text{ erg }-13{\cdot}6\text{ eV.}$$

4. *The energy of an electron in second and third orbit of the H-atom is* $-5{\cdot}42\times10^{-12}$ *ergs and* $-2{\cdot}41\times10^{-12}$ *ergs. respectively. Calculate the wavelength of the emitted radiation when the electron drops from third to the second orbit.*

Sol. Energy of 3rd orbit $=E_3=-2{\cdot}41\times10^{-12}$ ergs.
Energy of 2nd orbit $=E_2=-5{\cdot}42\times10^{-12}$ ergs.

We know that, $E_3-E_2=h\nu=\dfrac{hc}{\lambda}$

$$-2{\cdot}41\times10^{-12}+5{\cdot}42\times10^{-12}=\frac{6{\cdot}6\times10^{-27}\times3\times10^{10}}{\lambda}$$

or $$\lambda=\frac{6{\cdot}6\times10^{-27}\times3\times10^{10}}{3\;01\times10^{-12}}=6{\cdot}6\times10^{-5}\text{ cm}=6{\cdot}6\times10^{-7}\text{ metre}$$

5. *Calculate the wavelength in Angstroms of the photon that is emitted when an electron in the Bohr orbit* $n=2$ *return to the orbit* $n=1$ *in the hydrogen atom. The ionisation potential of the ground state of hydrogen atom is* $2{\cdot}17\times10^{-11}$ *ergs per atom.* **[I. I. T. 1982]**

Sol. $E_1=-2{\cdot}17\times10^{-11}$ ergs $\left(\because\ E=-\dfrac{2n^2z^2e^4m}{n^2h^2}\right)$

$$\therefore\ E_n=\frac{E_1}{n^2}\ (h=6{\cdot}6256\times10^{-27}\text{ erg sec, }c=3\times10^{10}\text{ cm/sec})$$

$$\therefore\ E_2=-\frac{2{\cdot}17\times10^{-11}}{2^2}=-\frac{2{\cdot}17\times10^{-11}}{4}\text{ ergs}$$

$$E_2-E_1=h\nu=\frac{hc}{\lambda}=(-)\frac{2{\cdot}17\times10^{-11}}{4}+\frac{2\;17\times10^{-11}}{1}$$

$$=\frac{6{\cdot}6256\times10^{-27}\times3\times10^{10}}{\lambda}$$

$$\therefore\quad \lambda=\frac{6{\cdot}6256\times10^{-27}\times3\times10^{10}\times4\times10^{8}}{3\times2{\cdot}17\times10^{-11}}=1221\ \text{Å}.$$

1.20. Bohr-Bury Scheme

(i) The maximum number of electrons in any orbit is given by $2n^2$ where n is the orbit number.

TABLE

Orbit	*Orbit no.* (*n*)	*Maximum no. of Electrons.*
K	1	$2 \times 1^2 = 2$
L	2	$2 \times 2^2 = 8$
M	3	$2 \times 3^2 = 18$
N	4	$2 \times 4^2 = 32$ etc.

(ii) The outermost shell in an atom shall not have more than 8 electrons and the penultimate (shell just before the outermost shell) shall not have more than 18 electrons.

(iii) It is not necessary for an orbit to be completed before other commence to be formed. In fact, a new orbit begins when the outermost orbit attains 8 electrons.

(iv) The outermost orbit cannot have more than two electrons and the penultimate orbit can not have more than 18, so long as the next inner orbit in each has not received the maximum number of electrons as required by (i) and (ii) above.

The electronic arrangement of few elements on the basis of above rule are given below :

TABLE

Element	*Atomic Number*	*No. of extra nuclear electrons*	*Number of orbits*						
			1	2	3	4	5	6	7
He	2	2	2						
Ne	10	10	2	8					
A	18	18	2	8	8				
Ba	56	56	2	8	18	18	8	2	
Hg	80	80	2	8	18	32	18	2	
Rn	86	86	2	8	18	32	18	8	

1.21. Sommerfeld Extension over Bohr Theory

Although Bohr's theory accounted for the positions of the lines in the optical spectrum of hydrogen. It did not account for the splitting of these lines into groups of finer lines when spectroscopes of higher resolving power were applied. To account for such structure Sommerfield modified the Bohr's theory to include elliptical electron orbit as well as circular. According to Sommerfeld;

(i) Each orbit except the first is made up of sub-orbits which may be circular or elliptical

(ii) The various sub-orbits of an orbit have very slightly different energies. The energies of sub-orbits are also quantized. He introduced subsidiary quantum number, K. So that

$$\frac{\text{Principal quantum number}}{\text{Subsidiary quantum number}} = \frac{n}{K}$$

$$= \frac{\text{Length of major axis of a sub-orbit.}}{\text{Length of minor axis of the same sub-orbit.}}$$

1.22. Draw Backs

1. It could not give exact number of lines observed in fine structure.
2. It gives no information about the relative intensities of the fine lines.
3. The exact definition of position and momentum is contrary to the uncertainty principle.
4. Sommerfeld theory was able to explain the spectrum of H electron. The theory fails when system has got more than one electron. Complex system can not be explained by this theory.
5. It does not give any idea about arrangement of various electrons in the system.

1.23. Nuclear Stability

Stable nuclei of lighter elements contain equal number of protons and neutrons; for example; ${}^{40}_{20}Ca$ has 20 protons and 20 neutrons i.e. proton to neutron ratio is 1 : 1. But in the case of heavier elements the neutron to proton ratio is greater than 1. In case of ${}^{136}_{56}Ba$ there are 56 protons and 82 neutrons, almost 50% more neutrons than protons.

It looks impossible that in a small area of the nucleus, protons are lying side by side and are held together. It is explained on the assumption that nuclear forces which are not governed by conventional laws of physics, operate in small range which corresponds to nuclear radius. Nuclear forces of attraction between similar particles are much greater than the forces of repulsion. In the formation of nucleus, some mass of the nucleus is converted into energy and this holds the nucleons together in the nucleus. There is an ample evidence to show that the mass of the atom is less than the sum of the massess of protons, neutrons and electrons.

1.24. Odd even Rules of Nuclear Stability

A survey of the naturally occurring stable nuclides, has found that nuclei containing *even number of protons and even number of neutrons are much more common than others.* Nuclei with odd nnmber of protons and even number of neutrons and vice versa are also common but those containing odd numbers of both protons and neutrons are less in common.

TABLE

Number of Stable Nuclide

Mass number	*Neutrons*	*Protons*	*Number of nuclides*
Even	(i) Even	Even	166
	(ii) Odd	Odd	8
Odd	(i) Even	Even	67
	(ii) Odd	Odd	53

The six nuclides $^{12}_{6}C$, $^{16}_{8}O$, $^{24}_{12}Mg$, $^{28}_{14}Si$, $^{40}_{20}Ca$ and $^{56}_{26}Fe$ which have even-even number of protons and neutrons constitute 80% of the earth's crust.

1.25. Orbit, Shell, Energy Level

It is the path through which electrons move with certain energy. Orbits are represented by *K* (Ist orbit), *L* (2nd-orbit), *M* (3rd orbit) etc. in spectroscopy. The maximum number of electrons in any orbit is $2n^2$ where n is the number of orbit.

Orbit	*Maximum electrons* ($2n^2$)
1 (*K*-shell)	$2\times1^2=2$
2 (*L*-shell)	$2\times2^2=8$
3 (*M*-shell)	$2\times3^2=18$ etc.

1.26. Sub-orbit, Sub-shell, Sub-energy Level

Each orbit excepting the first orbit is divided. The number of sub-orbits is equal to the number of orbits. They are represented by *s* (sharp), *p* (principal), *d* (diffuse) and *f* (fundamental) in spectroscopy. The maximum number of electrons in any sub-orbit is $(4n-2)$ or $(4l+2)$ where n = principal quantum number, l = azimuthal quantum number.

TABLE

Orbits	*Sub-orbits*	*Maximum no. of electrons on sub-orbits*
(n)	(l)	$(4n-2), (4l+2)$
1 (K-shell)	$(l=0)$	$4\times1-2, 4\times0+2=s^2$
2 (L-shell)	$p(l=1)$	$4\times2-2, 4\times1+2=p^6$
3 (M-shell)	$p, d(l=2)$	$4\times3-2, 4\times2+2=d^{10}$

The s^2, p^6, d^{10} and f^{14} electrons are present in s, p, d, and f sub-shell.

1.27. Orbital

The rapidly moving electrons would occupy effectively the entire space around the nucleus but at any given instant the electrons would be found somewhere in a three dimensional space best described by points of highest probability. The shape and size of this region in space around the nucleus where the probability of finding an electron with certain energy is maximun, is called an *orbital*. An electron can be anywhere within an orbital at any given time, although it tends to occuppy certain portions of its orbital to a greater extent than other portions. Each sub-shell excepting s-sub-shell is divided. p-sub-shell contains 3-orbitals, (p_x, p_y and p_z), d-sub-shell contains 5-orbitals ($d_{xy}, d_{yz}, d_{zx}, d_{z^2}$ and $d_{x^2-y^2}$) and $f-$ sub-shell contains 7-orbitals.

s-orbitals : The electron charge cloud associated with an electron in an s-orbital is spherically symmetrical.

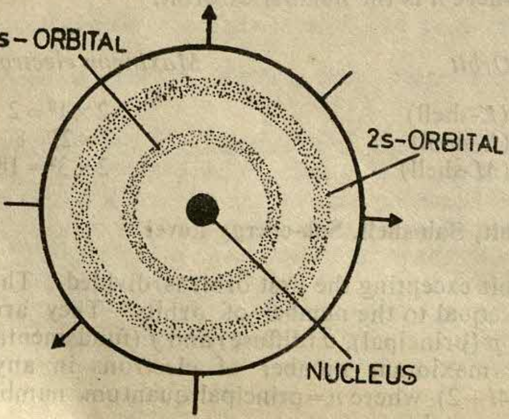


Fig. 1.8. Spherically symmetrical s-orbital charge cloud.

p-orbitals : There are three orbitals for each p sub-shell. If three perpendicular axes p_x, p_y, and p_z are chosen, each p-orbital is aligned along one or other of the axes. They are correspondingly termed p_x, p_y and p_z orbital. Hence p-orbitals are dumb bell shape.

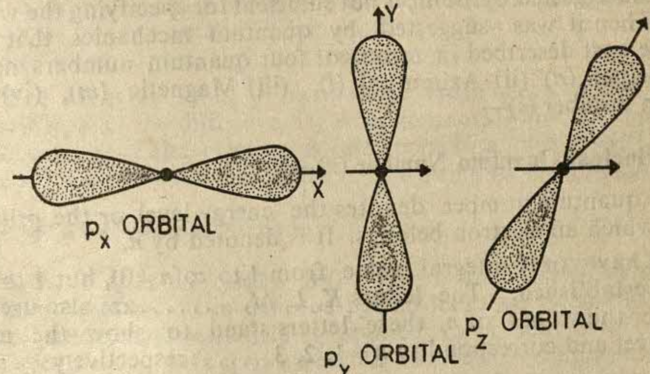


Fig. 1.9. p_x, p_y, p_z orbital charge clouds

d-orbitals : The shape of d-orbital electron clouds are more complex than either s or p orbitals. Every d- sub-shell contains five d-orbitals with the shapes shown below. It has got double dumb-bell shaped.

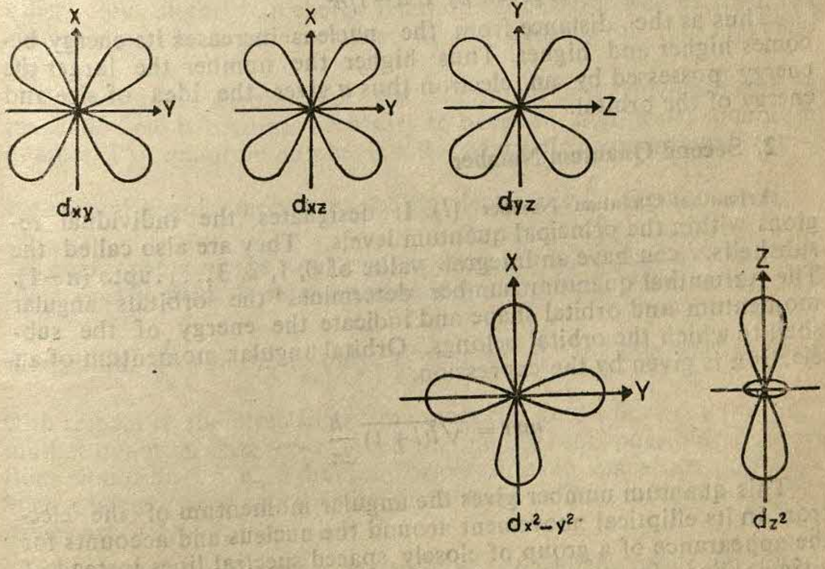


Fig. 1.10. d-orbital charge clouds

1.28. Quantum Number

We have seen that Bohr's theory could not explain the existence of fine structure in the H-spectrum. The appearance of several lines in the H-spectrum, therefore indicates that only one quantum number, *n*, as suggested by Bohr, is not sufficient for specifying the various lines. Then it was suggested by quantum mechanics that electrons are best described in terms of four quantum numbers namely (i) Principal (*n*) (ii) Azimuthal (*l*), (iii) Magnetic (*m*), (iv) spin quantum number (*s*)—

1. Principal Quantum Number (*n*)—

This quantum number denotes the energy level or the principal shell to which an electron belongs. It is denoted by *n*.

n can have only integral value from 1 to $\infty (n \neq 0)$, but 1 to 7 so far been established. The letters *K*, *L*, *M*,........are also used to designate the values of *n*. these letters stand to show the major energy level and correspond to $n=1, 2, 3$ ......respectively

Then when $n=1, 2, 3, 4$....the letter used are *K*, *L*, *M*, *N*,.... respectively. If for an electon $n=3$, it resides in the *M* shell, *n* gives the idea of the shell and is the same integer as suggeted by Bohr

$$mvr = n.\frac{h}{2\pi}.$$

The relationship between principal quantum number *n* and energy *E* from Bohr theory is given by $E \; \alpha - 1/n^2$.

Thus as the distance from the nucleus increases its energy becomes higher and higher. Thus higher the number the larger the energy possessed by an electron thus *n* gives the idea of size and energy of the orbital.

2. Second Quantum Number

Azimuthal Quantum Number (*l*). It designates the individual regions within the principal quantum levels. They are also called the subshells. *l* can have an integral value of 0, 1, 2, 3,....upto $(n-1)$. The Azimuthal quantum number determines the orbitals angular momentum and orbital shape and indicate the energy of the subshell to which the orbital belongs. Orbital angular momentum of an electron is given by the expression.

$$mvr = \sqrt{l(l+1)}\,\frac{h}{2\pi}$$

This quantum number gives the angular momentum of the electron in its elliptical movement around the nucleus and accounts for the appearance of a group of closely spaced spectral lines instead of a single line, in the spectra of hydrogen or hydrogen like atoms

(He^+, Li^{2+}, Be^{3+}.). If the prinicipal quantum number $n=1$, l can have only one value equal to zero (i.e., $l=0$) If $n=2$, l can have two values ($l=0$ and $l=1$). If $n=3$, l can have three values ($l=0$, $l=1$, and $l=2$). If $n=4$, l can have four values ($l=0$, $l=1$, $l=2$ and $l=3$).

If n gives the major energy levels (or shell) l gives the possible sub-levels or (sub-shells). When $l=0, 1, 2, 3, 4 \ldots$ the sub-shells are referred to as $s, p, d, f, g \ldots\ldots$ respectively.

(The term s, p, d, f have come from spectroscopy s=sharp, p=principal,, d=diffusion, f=fundamental) *For example*, when $n=4$, and $l=2$ the electron is said to be in a $4d$ sub-shell, similarly when $n=4$ and $l=0$ the electron is said to be in $4s$-sub-shell.

3 Third Quantum Number

Magnetic Quantum Number (m) : This is also known as *orientation quantum number*. It is denoted by the letter m. Zeeman found that when a strong magnetic field is applied to a source of spectrum, each spectral line gets split up into a number of separate lines. This phenomenon is called **Zeeman effect.** If the spectrum is viewed in the same direction as the applied magnetic field, each line is seen to be split up into two components. Both of these are found to be circularly polarised but in the opposite directions. If on the other hand, the spectrum is viewed in a direction at right angles of the magnetic field, each line is seen to be split up into three lines. The middle line is polarised in a direction parallel to the magnetic field and the other two lines are polarised at right angles to it. The additional lines differ only slightly in energy from one another as well as from the original line which appears alone in the absence of the magnetic field.

In order to account for the additional lines which appears in magnetic field it becomes necessary to have an additional quantum number. This quantum number is called **Magnetic quantum number (m)**.

If the total angular momentum of the electron is $\frac{h}{2\pi}$ then $\frac{h}{2\pi}$ gives the components of the total angular momentum in the direction of the magnetic field. If this component is quantised, the total angular momentum $\frac{h}{2\pi}$ can have only a definite of possible inclinations with respect to the direction of the magnetic field Suppose the Azimuthal quantum number is 2 then the number of possible inclinations would be 5. i. e., 5 different orientations in space are possible. Such a behaviour is called space quantization. The corresponding m values are $+2, +1, 0, -1, -2$.

The possible value which m can have depended upon the total angular momentum i. e., on the azimuthal quantum l for any value of l there are $(2l+1)$ values of m. These range lie from -1 through 0 to $+1$. *Thus making a total* of $(2l+1)$ values.

If $l=0$ (i.e., the sub-shell is s), there is only one value of m namely $m=0$; If $l=1$ (i.e., subshell is p) m can have three values i.e. $m=1$, 0 and $+1$. Similarly if $l=2$ m can have five values i.e., $m=-2, -1, 0, +1, +2$.

Thus s subshell will have 1, p sub-shell will have 3, d sub-shell will have 5 and f subshell will have 7 possible values of m.

The electrons having the same value of n and l but different value of m will have different energies. However, these energies differ only slightly from each other.

4. Fourth Quantum Number

Spin Quantum Number (s). It defines the angular momentum of the spin of the electron. If is denoted by s. It arises from the spectral evidence that an electron in its motion around the nucleus in an orbit also rotates or spins about its own axis. The electron can spin clockwise or anti-clockwise. Therefore, two values of s are possible. Since quantum numbers can differ from one another only by integers, s can have the values $+\frac{1}{2}$ or $-\frac{1}{2}$ depending upon whether the electron spins in one direction or in the other, the two values are generally written as $\underset{+\frac{1}{2}}{\uparrow}$ and $\underset{-\frac{1}{2}}{\downarrow}$

TABLE

The four quantum numbers describing an electronic energy state :

Quantum No.	*Symbol*	*Allowed value*	*Function*
Principal	n	1, 2, 3, ...	Governs the *energy* and *size* of the orbital.
Azimuthal or Subsidiary	l	$(n-1)(n-2)$ 0	Governs the shape of the orbital and the electronic angular momentum.
Magnetic.	m	$\pm l, \pm(l-1)$ 0	Governs the directions of an orbitals and the electrons behaviour in a magnetic field.
Spin	s	$\pm\frac{1}{2}$	Governs the axial angular momentum of the electron.

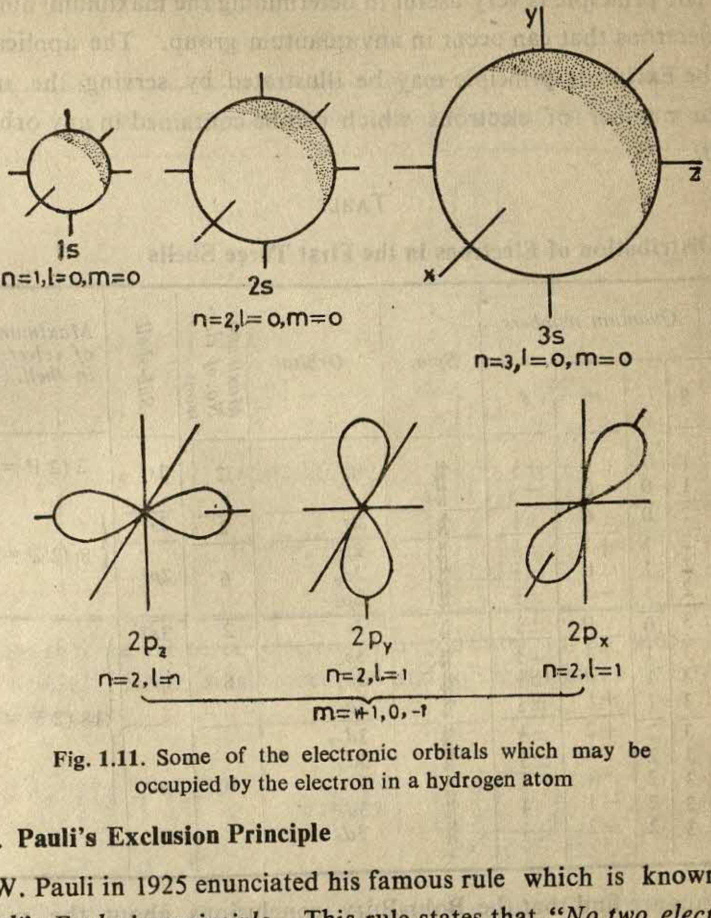


Fig. 1.11. Some of the electronic orbitals which may be occupied by the electron in a hydrogen atom

1.29. Pauli's Exclusion Principle

W. Pauli in 1925 enunciated his famous rule which is known as "*Pauli's Exclusion principle.* This rule states that "*No two electrons of a particular atom can have all the values of four quantum numbers same.* Thus in the same atom, any two electrons may have three (n, l and m) quantum numbers identical but the fourth (s) must be different.

ILLUSTRATION : Helium (*He*) has got two electrons. For both electrons of Helium, $n=1$, $l=0$, $m=0$ but spin will be $+\frac{1}{2}$ or $-\frac{1}{2}$. Thus the value of the fourth quantum number is different.

i.e.	n	l	m	s
	1	0	0	$+\frac{1}{2}$
	1	0	0	$-\frac{1}{2}$

The principle is very useful in determining the maximum number of electrons that can occur in any quantum group. The application of the Exclusion principle may be illustrated by serving the maximum number of electrons which can be contained in any orbit or shell.

TABLE

Distribution of Electrons in the First Three Shells

Principal shell.	*Quantum numbers*				*Spin.*	*Orbital*	*Maximum No. of electrons*	*Sub-shell*	*Maximum No. of electrons in shell.* ($2n^2$)
	n	*l*	*m*	*s*					
K	1	0	0	$+\frac{1}{2}$	⇅	1*s*	2	$1s^2$	$2\ (2 \cdot 1^2 = 2)$
	1	0	0	$-\frac{1}{2}$	⇅				
L	2	0	0	$\pm\frac{1}{2}$	⇅	2*s*	2	$2s^2$	$8\ (2 \cdot 2^2 = 8)$
	2	1	+1	$\pm\frac{1}{2}$	⇅	$2p_x$	6	$2p^6$	
	2	1	0	$\pm\frac{1}{2}$	⇅	$2p_y$			
	2	1	−1	$\pm\frac{1}{2}$	⇅	$2p_z$			
M	3	0	0	$\pm\frac{1}{2}$	⇅	3*s*	2	$3s^2$	$18\ (2 \cdot 3^2 = 18)$
	3	1	+1	$\pm\frac{1}{2}$	⇅	$3p_x$	6	$3p^6$	
	3	1	0	$\pm\frac{1}{2}$	⇅	$3p_y$			
	3	1	+1	$\pm\frac{1}{2}$	⇅	$3p_z$			
	3	2	+2	$\pm\frac{1}{2}$	⇅	$3d_{xy}$	10	$3d^{10}$	
	3	2	+1	$\pm\frac{1}{2}$	⇅	$3d_{yz}$			
	3	2	0	$\pm\frac{1}{2}$	⇅	$3d_{xz}$			
	3	2	−1	$\pm\frac{1}{2}$	⇅	$3d_{z^2}$			
	3	2	−2	$\pm\frac{1}{2}$	⇅	$3d_{x^2-y}$			

Thus we find that the Bohr-Bury conclusions about the maximum number of electrons in different electronic levels given by **$2n^2$** is confirmed by Pauli's exclusion principle.

1.30. Hund's Rule of Maximum Multiplicity

It states that the electrons in any sub-shell (s, p, d or f) occupy the orbitals singly with parallel spins before pairing in any orbitals commences.

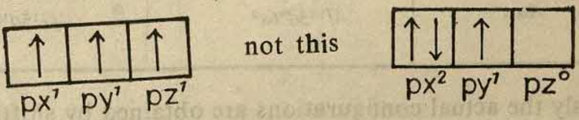
In other words, the pairing must begin with the entry of second electron in the *s*-orbital, the fourth electron in the '*p*'-orbital the sixth electron in the *d*-orbital and eight electron in the *f*-orbital.

The arrangement of electrons in first six elements under Hund's rule of maximum multiplicity can be shown as follows :

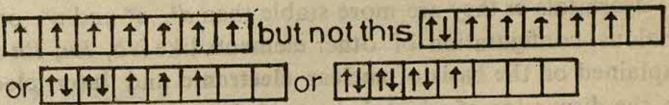
TABLE

Element	*At. No.*	*Electronic Configuration*	*Electronic distribution in orbital*
H	1	$1s^1$	1S' ↑
He	2	$1s^2$	$2S^2$ ↑↓
Li	3	$1s^22s^1$	↑↓ 2S' ↑
Be	4	$1s^22s^2$	↑↓ $2S^2$ ↑↓
B	5	$1s^22s^22p^1 2p_y^0 2p_z^0$	↑↓ ↑↓ 2px' ↑
C	6	$1s^22s^22p_x^12p_y^12p_z^0$	↑↓ ↑↓ 2px' py' ↑ ↑

Thus if there are three electrons in *p*-orbital in an atom then each orbital will be singly occupied and the arrangement in ground state will be as :



If there are 7 electrons in 4*f*- orbitals, the arrangement in the ground state will be :



This rule is found to be quite helpful in describing the position of an electron.

(*a*) *Electrons tend to avoid being in the same orbital as far as possible and* (*b*) *Electrons tend to have the same spin if they are the equivalent orbitals.* Sub-orbitals (e.g., s, p_x, p_y, p_z........) tend to become completely filled or half filled since such orbitals are more stable than any other orbital.

1.31. Anomalous Configurations

A study of the table shows that the actual (i.e., experimental) configurations as given in the table of some transition elements (*d*-block elements) are different from their expected configurations as shown below :

TABLE

Series	*Element with atomic number.*	*Expected valence shell configuration*	*Actual valence shell configuration*
3*d* series	Cr_{24}	$3d^4 4s^2$	$3d^5 4s^1$
	Cu_{29}	$3d^9 4s^2$	$3d^{10} 4s^1$
4*d* series	Nb_{41}	$4d^3 5s^2$	$4d^4 5s^1$
	Mo_{42}	$4d^4 5s^2$	$4d^5 5s^1$
	Ru_{44}	$4d^6 5s^2$	$4d^7 5s^1$
	Rh_{45}	$4d^7 5s^2$	$4d^8 5s^1$
	Pd_{46}	$4d^8 5s^2$	$4d^{10} 5s^0$
	Ag_{47}	$4d^9 5s^2$	$4d^{10} 5s^1$
5*d* series	Pt_{78}	$4f^{14} 5d^8 6s^2$	$4f^{14} 5d^9 5s^1$
	Au_{79}	$4f^{14} 5d^9 6s^2$	$4f^{14} 5d^{10} 6s^1$

Obviously the actual configurations are obtained by shifting one or two electrons from *ns* to $(n-1)$ *d*-orbitals. Such type of shifting in case of some elements like *Cr*, *Cu*, *Mo*, *Pd*, *Ag* and *Au* can be explained on the basis of the concept that half filled or completely filled $(n-1)$ *d*-orbitals as they are more stable than d^4, d^8 and d^9 orbitals. Anomalous configuration of other elements like *Nb*, *Ru*, *Rh* and *Pt* are explained on the basis of **nuclear electronic** and **inter electronic forces**, the discussion of which is beyond the scope of the syllabus.

1.32. The Aufbau Principle

Aufbau is a German word meaning '*building up*'. *According to this principle the orbitals are filled up in the order of increasing energy. i.e., the orbital with the lowest energy is filled up first while* *that of the highest energy filled up in the end.* The energy of various orbitals increases in the order given below :

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p$$
$$< 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f \ldots\ldots$$

——————————Energy Increases——————→

As a working rules for filling orbitals are given below :

Rule 1. A new electron enters the orbital for which $(n+l)$ (i.e., principal + azimuthal quantum number) is minimum, e.g,, if we consider 3*d* and 4*s* orbitals, the electron will first enter 4*s*-orbital in preference to 3*d*-orbitals. This is because of the fact that the value of $(n+l)$ for 4*s* orbital is less $(4+0=4)$ than that for 3*d*-orbital $(3+2=5)$.

Rule 2. In case of orbitals for which $(n+l)$ values are the same, the new element enters the orbital for which *n* is minimum, e.g., if there is a choice for the electron to enter 3*d* and 4*p* orbital for both of which $(n+l)$ values are the same $(=3+2=5,\ 4+1=5)$, the electron will prefer to go to 3*d*-orbital, since *n* is lower for this orbital.

The value of $n=1, 2, 3, 4 \ldots\ldots$ etc. and $l=0(s)$, $1(s)$ $2(d)$ and $3(f)$.

The above fact is illustrated in the table below :

TABLE

n	*l*	$n+l$	*Orbitals*
1	0	$1+0=1$	1*s*
2	0	$2+0=2$	2*s*
	1	$2+1=3$	2*p*
3	0	$3+0=3$	3*s*
	1	$3+1=4$	3*p*
	2	$3+2=5$	3*d*
4	0	$4+0=4$	4*s*
	1	$4+1=5$	4*p*

According to Rule I

The electron occupies 1*s* because the value of 1*s* $(n+l)$ is less than 2*s*,. Similarly electrons occupy 2*p*. The value of $(n+l)$ for 2*p* and 3*s* is the same.

Hence According to Rule II The electrons occupy the lower value of '*n*'. Hence electrons occupy 2*p* then they occupy 3*s*. In this way, the different orbitals are filled up with electrons. The relative stability of various orbitals and the sequence in which the electrons occupy the various orbitals are as follows :

1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*,
5*p*, 6*s*, 4*f*, 5*d*, 6*p*, 7*d*, 5*f*, 6*d*, 7*p*,

The energy level diagram is shown below :

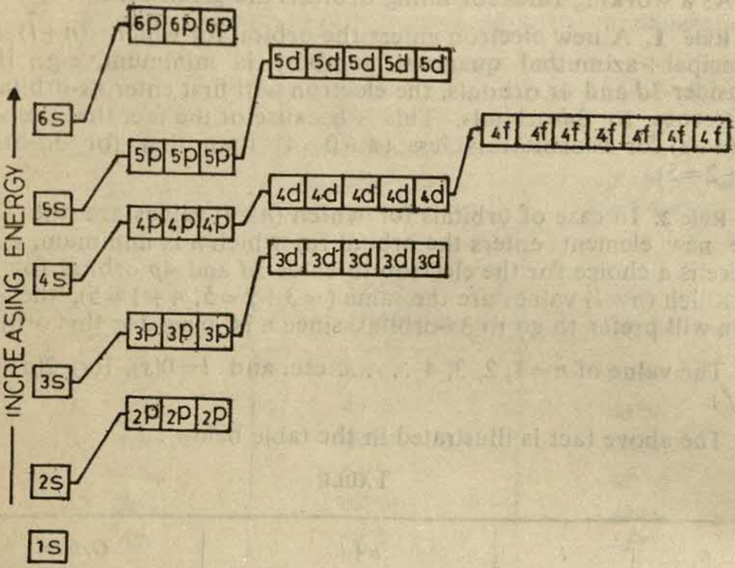


Fig. 1.12. Energy level diagram of Poly-electron atoms

Example : (1) In the case of potassium (Atomic. No. 19) the nineteenth electron might enter 3*d* or 4*s* sub-shells. The working rule for this is that the electron will enter the sub-shell having a lower value of $n+l$. For 3*d*, $n=3$ and $l=2$ and therefore $n+l=3+2=5$.

For 4*s*, $n=4$ and $l=0$ and therefore $n+l=4+0=4$

Hence the electron will enter the 4*s* sub-shell in preference to 3*d*.

1.33. Exceptions to the Aufbau's Principle

1. A single 5*d* electron is added before any 4*f*-orbital is occupied. Here $n+l=7$ in both the cases the electron must occupy 4*f* orbital. After that the remaining nine 5*d*-electrons enter this sub-shell after the 4*f* sub-shell has been completely filled with electrons. Similar is the case with 6*d* and 5*f*.

The electron must occupy 5*f*-orbital but actually one or two electrons go to 6*d*-orbital. *This is based on the fact that 4f and 5d sub-shells of energy are very close to each other and 5f and 6d sub-shells are even still closer.*

Example : Lanthanum (*La*) Atomic Number 57 : $1s^2$, $2s^2\ 2p^6$, $3s^2$

$$3p^6\ 3d^{10},\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 6s^2\ \boxed{4f^0\ 5d^1}.$$

1.3.3 Atomic Structure of Elements

The atomic structure of an element means to show the arrangement of electrons, protons and neutrons in an atom.

6. *Write down the atomic structure of*

(a) ${}^{23}_{11}Na$ (b) O^{-2} *and* (c) Mg^{+2}

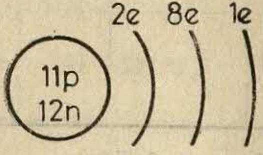


Fig. 1.11

Atomic structure of sodium

Sol. (a) Sodium (*Na*) At. no. = 11 = No. of protons or No. of electrons.

No. of neutrons = 23 − 11 = 12

Electronic configuration – $1s^2\ 2s^2\ 2p^6\ 3s^1$

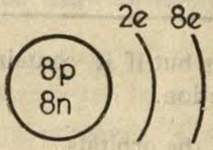


Fig. 1.12

Atomic structure of Oxide ion

(b) No. of protons = 8, No. of electrons = 8 + 2 = 10

Electronic configuration—$1s^2\ 2s^2\ 2p^6$
No. of neutrons = 16 − 8 = 8

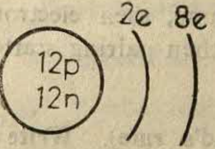


Fig. 1.13

Atomic structure of Magnesium ion

(c) No. of protons = 12, No. of electron = 12 − 2 = 10

Electronic configuration—$1s^2\ 2s^2\ 2p^6$

No. of neutrons = 24 − 12 = 12

1.34. Electronic Configuration

The electronic configuration of an element means to show the arrangement of electrons. This can be written as :

(i) *orbitwise*, (ii) *inert gas wise* (iii) *sub-orbit wise* and (iv) *orbital wise or Box type*. While writing the electronic configuration of the elements, the following rule is a guide line.

(a) The maximum number of electrons in any orbit is $2n^2$.

K – orbit : $n=1$ Maximum electrons $= 2\times 1^2 = 2$
L – orbit : $n=2$ Maximum electrons $= 2\times 2^2 = 8$

(b) The orbit is divided into sub-orbit as s, p, d and f and these are denoted by azimuthal quantum number (l) 0, 1, 2 and 3 respectively. The maximum number of electrons on different orbitals are s^2, p^6, d^{10}, f^{14}.

(c) The sub-orbit shows different orientation in magnetic field, which is called magnetic quantum number (m). The number of orbitals in sub-shells are—

TABLE

Sub-orbits (s)	1 Orbital	Sub-orbits (d)	5 orbitals
Sub-orbits (p)	3 orbital $p_x\ p_y\ p_z$	Sub-orbit (f)	7 orbitals

(d) Each orbital contains one or two electrons but if it contains two electrons, then their spin is in opposite direction.

(e) The electrons occupy the lowest energy of the orbitals.

(f) No. two electrons of a particular atom can have all the four values of quantum number same.

(g) If the energy of different orbitals is the same, then electrons occupy different orbital singly having same spin then pairing started with opposite spin.

(h) Generally do not write d^4 or d^9 (see Hund's rule). Write d^5 or d^{10} by taking electrons from $4s$ or $5s$ in case of elements.

(i) In case of writing the electronic configuration of ions of d-block elements, remove the electrons first from 's'-sub-shell then from d-sub-shell. But in case of ions of other block elements, the electrons are added or subtracted from the outermost orbit.

7. *Write down the electronic configuration of (i) Na (ii) Cl in terms of (a) orbit, (b) sub-orbit, (c) Inert gas and (d) orbital or box type.*

Sol.

TABLE

Element	*At. No.*	*Electronic configuration*			
		Orbit-wise	*Inert gas wise*	*Sub-orbit wise*	*orbital wise*
Sodium (Na)	11	$2K$, $8L$, $1M$	$\boxed{Ne}\ 3s^1$	$1s^2 2s^2 2p^6 3s^1$	[↑↓] [↑↓] [↑↓|↑↓|↑↓] [↑] 1s 2s 2p 3s
Chlorine (Cl)	17	$2K$, $8L$, $7M$	$\boxed{Ne}\ 3s^2\ 3p^5$	$1s^2 2s^2 2p^6$ $3s^2 3p^5$	[↑↓] [↑↓] [↑↓|↑↓|↑↓] [↑↓] [↑↓|↑↓|↑] 1s 2s 2p 3s 3p

Note : Generally the electronic configuration of the elements are written as sub-orbit wise.

1.35. How To Write the Electronic Configuration of Ions ?

In case of cations (positively charged) subtract the number of charges and in case of anions, add the number of charges i.e., the total number of electrons in the case of ions.

(i) Oxide ion (O^{-2}), total electrons $= 8 + 2 = 10$
Electronic Configuration (E. C.) $= 1s^2\ 2s^2\ 2p^6$

(ii) Aluminium ion (Al^{+3}) :

Total electrons $= 13 - 3 = 10$, E. C. $1s^2\ 2s^2\ 2p^6$

(iii) Ferrous ion (Fe^{+2}) : Total electrons $= 26 - 2 = 24$

Since it is a *d*-block element and hence electrons are removed from first '*s*'-sub-shell then from '*d*'-sub-shell.

$$Fe^{+2} = 26 - 2 = 24$$

The electronic configuration can be written as :

(a) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4\ 4s^2$
(b) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$
(c) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$

But (a) and (b) are incorrect because electrons have not been removed from '*s*'-sub-shell, hence (c) is correct.

(iv) Cupric ions (Cu^{+2}). Total electrons $= 29 - 2 = 27$

Its electronic configuration can be written as :

(a) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$

(b) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$

(c) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^1$

But (a) and (c) are incorrect because electrons have not been removed from *s*-sub-shell. In case of ion. d^4 or d^9 can be written.

The electronic configuration of some *d*-block elements and ions are given below :

TABLE

Element or ions	*At. No.*	*No. of Electrons.*	*Electronic configuration.*
Fe	26	26	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6 4s^2$
Fe^{+2}		24	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6$
Fe^{+3}		23	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5$
Cr	24	24	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$
Cr^{+3}		21	$1s^2, 2s^2 2\mathrm{p}^6, 3s^2 3p^6 3d^3$
Mn	25	25	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^2$
Mn^{+2}		23	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5$
Co	27	27	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^7, 4s^2$
Co^{+2}		25	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^7$
Cu	29	29	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^1$
Cu^{+}		28	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}$
Cu^{+2}		27	$1s^2, 2s^2 2p^7, 3s^2 3p^6 3d^9$.

INFORMATION FROM ELECTRONIC CONFIGURATION

1.36 (A) : Block

The outermost sub-shell in energy sequence is called the block of the element.

TABLE

Element	*At. No.*	*E. C.*	*Outermost orbital*	*Block*
Na	11	$[Ne]\ 3s^1$	*s*	*s*
Cl	17	$[Ne]\ 3s^2 3p^5$	*p*	*p*
Fe	26	$[Ar]\ 4s^2 3d^6$	*d*	*d*
Ce	58	$[Xe]\ 6s^2 5d^4 4f^1$	*f*	*f*

The general electronic configuration of the element with block is given below :

Block	*General electronic configuration*
(i) *s*-block elements	ns^1 to ns^2
(ii) *p*-block elements	$ns^2 np^{1-6}$
(iii) *d*-block elements	$ns^{1-2}\ (n-1)\ d^{1-10}$
(iv) *f*-block elements	$ns^2\ (n-1)\ d^{1-10}\ (n-2)\ f^{1-14}$

1.36 (B) : Valence Electrons

The total number of electrons in the outermost orbit is called valence electrons. In case of *p*-block elements summation of *'s'* and *p*-sub-shell electrons and in case of *d*-block elements summation of electrons on *'s'* and *'d'*-sub-shell electrons are called valence electrons. If sum of number of electrons on *'s'* and *'d'*-sub-shell is more than 8 then valence electrons are equal to the number of electrons in the outermost orbit.

TABLE

Elements with At. no.	*Electronic configuration*	*Block*	*Valence Electrons*
Mg (12)	$1s^2,\ 2s^2 2p^6,\ 3s^2$	*s*	2
S (16)	$1s^2,\ 2s^2 2p^6,\ 3s^2 3p^4$	*p*	6 $(3s^2\ 3p^4)$
Cr (24)	$1s^2,\ 2s^2 1p^6,\ 3s^2 3p^6 3d^5,\ 4s^1$	*d*	6 $(3d^5\ 4s^1)$
Fe (26)	$1s^2,\ 2s^2 2p^6,\ 3s^2 3p^6 3d^6,\ 4s^2$	*d*	2 $(3d^6\ 4s^2)$*
Co (27)	$1s^2,\ 2s^2 2p^6,\ 3s^2 3p^6 3d^7,\ 4s^2$	*d*	2 $(3d^7\ 4s^2)$**
Cu (29)	$1s^2,\ 2s^2 2p^6,\ 3s^2 3p^6 3d^{10},\ 4s^1$	*d*	1 $(3d^{10}\ 4s^1)$***

***** In I.sc. stage the valency of an element can not be more than 8 (Octet rule) hence the valency can not be more than 8.**

1.36 (C) : Core or Kernel Electrons

The electrons excluding the valence electrons are known as core or Kernel electrons. The number of core electrons is equal to the number of electrons in the nearest inert gas elements.

For Example : ∵ core electron = (Total electron − valence electron)
For *Na.* $(Z = 11)$. valence—electron = 1
∴ core electron = 11 − 1 = 10

1.36 (D) : Penultimate Electrons

The electrons just before the outermost orbit are called penultimate electrons. The maximum number of electrons in penultimate orbit is 18.

TABLE

Element	*At. No.*	*Electronic configuration*	*Valence electrons.*	*Core electrons*	*Penultimate electrons*
Mg	12	$1s^3, 2s^2 2p^6, 3s^2$	2	10	8
P	15	$1s^2, 2s^2 2p^6, 3s^2 3p^3$	5	10	8
Fe	26	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6, 4s^2$	8	18	14
Ni	28	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^8, 4s^2$	2 or 10	26 or 18	16
Cu	29	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^1$	1 or 11	28 or 18	18

Note : If the penultimate orbit is incomplete i.e. it contains electrons less than inert gas atomic number, then the element shows variable valency as for example iron and nickel etc. in the table.

1.36. (E). Valency Electrons

The number of electrons taking part in bond formation is called valency electron. In most of the normal elements, the valency electrons and valence electrons are the same. In some cases they differ. See Table below.

TABLE

Element	*At. No.*	*Electronic Configuration*	*Valence electrons*	*Valency electrons.*
Na	11	$1s^2, 2s^2 2p^6, 3s^1$	1	1
Mg	12	$1s^2, 2s^2 2p^6, 3s^2$	2	2
Si	14	$1s^2, 2s^2 2p^6, 3s^2 3p^2$	4	4
O	8	$1s^2, 2s^2 2p^4$	6	2
Cl	17	$1s^2, 2s^2 2p^6, 3s^2 3p^5$	7	1

1.36. (F). Group

The valence electrons indicate the group of the elements. In case of '*s*' and '*p*' block, the sub-group is '*A*' and in case of '*d*' and '*f*' block, the sub-group is '*B*'. If sum of *s* and '*d*' electrons are equal to 8, 9, 10 then the elements belong to group VIII and if '*s*' plus '*p*' electrons equal to 8 then group is zero.

TABLE

Elements.	*At. No.*	*Electronic Configuration.*	*Valence electrons.*	*Block*	*Group*
P	15	$1s^2, 2s^2, 2p^6, 3s^2\ 3p^3$	5	*p*	VA
Ca	20	$1s^2, 2s^2, 2p^6, 3s^2\ 3p^6\ 4s^2$	2	*s*	IIA
Cr	24	$1s^2\ 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^5\ 4s^1$	6	*d*	VIB
Fe	26	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^6, 4s^2$	8	*d*	VIII
Cu	29	$1s^2\ 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^1$	1	*d*	IB
Ar		$1s^2, 2s^2\ 2p^6\ 3s^2\ 3p^6$	8	*p*	Zero

Note : Group VIII and group zero have got no sub-group.

1.36. (G). Period

The outermost orbit indicates the period of the element.

TABLE

Element	*At. No.*	*Electronic Configuration*	*Period.*
Al	13	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^1$	3
Mn	25	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^5\ 4s^2$	4

1.37. Wave Nature of electron (de-Broglie relation)

Louis de Broglie, a French Physicist introduced the idea of particle waves. An electron behaves both as a particle and as a wave. He combined the particle and wave nature of radiation as follows :

Since $E = h\nu$ (Planck equation) and
$E = mc^2$ (Einstein's mass-energy equation)
Equating both equation, we have energy $E = h\nu = mc^2$
or $h\nu = (mc.)\,c \quad [\because c = \lambda\nu]$

$$\text{or} \quad h\nu = (mc.).\ \lambda\nu \quad \therefore \quad \lambda = \frac{h}{mc} \qquad \ldots (1.9)$$

For an electron and other sub-atomic particles, he replaced the velocity of light c by the velocity of the particle v and wrote his equation $\lambda = \frac{h}{mv} = \frac{h}{p}$ .. (1.10)

where $p = mv$, momentum of the particle.

1.38. Heisenberg's Uncertainty Principle

A question arises due to dual nature (Wave-particle nature) of light, is it possible to know exactly where an electron is in space at some given instant ?" Werner Heisenberg in 1927 answered this question based on a principle enunciated as *'Unlestmmtheit'* in German. It means uncertainty, Indeterminacy, or Indefiniteness. *This principle of uncertainty states that the position and momentum of a particle can not be determined simultaneously with perfect accuracy. This is known as Heisenberg's uncertainty principle.* This is because the size of the electron is very small and the radiation of high energy with extremely small wavelength are required to detect it. In an attempt to do so, the direction and the speed of electron is affected. According to him we can measure position and momentum of such particles only within certain limits of accuracy. If Δv and Δx be the uncertainties in velocity and position respectively, combined uncertainly ($\Delta v.\ \Delta x$) could never be smaller than $\frac{h}{4\pi}$ or, $\Delta x.\ \Delta p \geqslant \frac{h}{4\pi}$

where Δp = uncertainty in momentum

The sign $\geqslant$ means that the product of Δp and Δx can be either greater than or equal to, but never smaller than $h/4\pi$. If Δp increases, Δx decreases and vice versa. This is equivalent to saying that momentum and position can not be determined simultaneously and accurately.

8. *Calculate the mass of a body moving with a velocity of* 10^8 *metre* sec^{-1} *and having de-Broglie wavelength equal to* $4{\cdot}2 \times 10^{-34}$ *m* Planck's constant, $h = 6{\cdot}627 \times 10^{-34}$ joule sec.

Sol. Velocity of the body $= v = 10^8$ ms^{-1}, wavelength of the body $\lambda = 4.2 \times 10^{-34}$ m; Planck's constant $h = 6{\cdot}627 \times 10^{-34}$ joule sec. The mass of the body can be calculated by using the relation.

$$\boxed{\lambda = \frac{h}{mv} \quad \text{or} \quad m = \frac{h}{\lambda v}} \qquad .. \quad (1.11)$$

Substituting the values, we get :

$$= \frac{6{\cdot}627 \times 10^{-34}\ \text{Js}}{4{\cdot}2 \times 10^{-34}\ \text{m} \times 10^{8}\ \text{ms}^{-1}} = \frac{6{\cdot}627 \times 10^{-34}\ \text{Js}^2}{4{\cdot}2 \times 10^{-26}\ \text{m}^2}$$

$= 1{\cdot}58 \times 10^{-8}$ kg.

Hence the mass of the body $= 1{\cdot}58 \times 10^{-8}$ kg.

1.39. Effective Nuclear Charge And Screening Effect

Effective Nucler Charge—It is the actual nuclear charge that is less than the screening effect due to other electrons in an atom. Effective Nuclear charge = Total Nuclear charge − screening effect.

Screening Effect : If an electron is to be removed from an atom, it is screened by the remaining electrons in the atom from the attractive influence of the nuclear positive charge and it makes easier to remove the electron. The approximate values of screening effect for the electrons present in different orbits are given below :

Orbits	*Screening effect*
1. For electrons outside the orbits considered.	Zero unit
2. From which the electrons are removed.	0·35 for each electron except the electron in consideration will have no contribution.
3. For each electron of s- and p-orbital of the penultimate orbits.	0·85 unit.
4. For each electrons of other inner orbits and *d*-orbitals.	1 unit

9. *Calculate the Effective nuclear charge of sodium.* (At. no. of $Na = 11$)

Sol. $Na\ (11) \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^1$

No. of units of positive charge in the nucleus $= +11$.

Screening effect (s) of (a) Two electrons of the 1st shell of $Na = 2 \times 1 = 2$ units charge.

(b) 8 electrons of 2nd shell $= 8 \times 0{\cdot}85 = 6{\cdot}80$ units.

Total $S = 2 + 6{\cdot}80 = 8{\cdot}80$ units.

∴ Effective Nuclear charge = Nuclear charge − Screening effect $= 11 - 8{\cdot}80 = 2{\cdot}2$ unit.

SOLVED PROBLEMS

10. *Find out the total number of electrons, protons and neutrons in* K, Na^+, O^{-2} ($^{39}_{19}K$, $^{23}_{11}Na$, $^{16}_{8}O$)

Sol.

Element or ions.	*At. No.*	*No. of protons*	*No. of Electrons*	*No. of Neutrons* $n=A-Z$
K	19	19	19	$n=39-19=20$
Na^+	11	11	$11-1=10$	$n=23-11=12$
O^{-2}	8	8	$8+2=10$	$n=16-8=8$

Note : (1) Z = number of protons. For neutral elements, atomic number is equal to the number of protons or electrons.

(2) For ions, number of protons = atomic number but no. of electrons are different from protons.

11. *A neutral element has mass number* 39. *It has got one neutron more than protons. Find out the number of electrons, protons and neutrons in this element.*

Sol. Let the number of protons in this element be x then number of neutrons be $x+1$. No. of neutrons = Mass No. – At. No.

or, $x+1=39-x$, or, $2x=38$, $\therefore\ x=19$.

Hence, no. of protons = 19 = No. of electrons (since it is neutral) No. of neutrons = 19 + 1 = 20.

12. *The atomic number of an element is* 35 *and atomic weight of two of its isotopes are* 79 *and* 81. *Find out* (*a*) *number of electrons in the outermost orbit* (*b*) *valency of the element* (*c*) *the number of neutrons and protons in nuclei of the two isotopes.*

Sol.

Term :	*Isotope* (*No.* 1)	*Isotope* (*No.* 2)
At. Wt.	79	81
At. No.	35	35
No. of protons	35	35
No. of electrons	35	35
No. of neutrons	$79-35=44$	$81-35=46$
Arrangement of Electrons.	2, 8, 18, 7	2, 8, 18, 7

(a) Hence the no. of electrons in the outermost orbit = 7.

(b) Valency in both cases = 1

(c) (No. 1) contains 44 neutrons and 35 protons and (no. 2) contains 46 neutrons and 35 protons.

13. *The molecular weight of an oxide of nitrogen be* 92. *Find out the total number of electrons in* (*a*) *one molecule* (*b*) *one mole of the oxide of nitrogen.* **(CEE 1980)**

Sol. Let the oxides of Nitrogen be :

Oxides	NO	N_2O	N_2O_3	NO_2	N_2O_4	N_2O_5
Mol. Wt.	30	44	76	46	92	108

Hence the oxide will be N_2O_4.

(a) No. of electrons in one molecule of $N_2O_4 = 7+7+8\times4 = 46$

(b) No. of electrons in mole of N_2O_4
$=$No. of electrons in one molecule of $N_2\ O_4$
$\times$No. of moles$\times$Avogadro's No. $= 46\times1\times6{\cdot}023\times10^{23}$

14. *The molecular weight of a saturated hydrocarbon be* 58. *Find out the total number of electrons in one molecule of the hydrocarbon.*

Sol. Let the formula of the saturated hydrocarbon be

$$C_nH_{2n+2} = 58.$$

$$12n+2n+2=58 \quad \text{or} \quad 14n=56 \quad \therefore\ n=4$$

Hence the formula of the hydrocarbon be C_4H_{10}. The total No. of electrons in one molecule of $C_4H_{10} = 4\times6+1\times10 = 34$.

15. *Find out the total number of electrons in* 1·6 *gm of methane.* **(T. S. Rajendra 1981; Roorkee '85)**

Sol. No. of electrons in one molecule of methane

$$(CH_4) = 6+4\times1 = 10$$

16 gm (1 mole) CH_4 contain $10\times6{\cdot}023\times10^{23}$ electrons.
1·6 gm. (0·1 mole) CH_4 contain $6{\cdot}023\times10^{23}$ electrons.

Alternatively

No. of electrons in 0·1 mole of CH_4

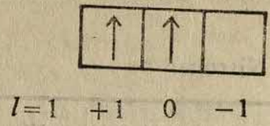
$=$No. of electrons in one molecule of $CH_4\times$No. of mole$\times N$
$=10\times0{\cdot}1\times6{\cdot}023\times10^{23} = 6{\cdot}023\times10^{23}$ electrons.

16. *Write down the values of all the quantum number for the last electron of carbon.*

Sol. At. wt. of $C = 6(1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0)$

Since, the last electron of carbon is present in $2p_y^1$

Hence $n=2$; $l=1$; $m=0$; $s=+\frac{1}{2}$ or $-\frac{1}{2}$



17. *How will you show with the help of quantum number that in the fourth orbit* ($n=4$) *the maximum number of electrons can be* 32 *?*

Sol. n (principal quantum no.) $=4$ then

l (azimuthal quantum no.) $= 0 \ldots\ldots\ldots (4-1)$

$= 0, 1, 2, 3$

Quite often instead of denoting l by the figures 0, 1, 2, 3........ referred to as s, p, d, f, respectively.

The maximum no. of electrons in s-sub-shell $=2$

The maximum no. of electrons in p-sub-shell $=6$

The maximum no. of electrons in d-sub-shell $=10$

The maximum no. of electrons in f-sub-shell $=14$

Hence the maximum number of electrons in the fourth orbit

$$=2+6+10+14=32$$

18. *Write the* (*a*) *atomic number* (*b*) *probable atomic mass and* (*c*) *total number of electrons for an atom*

$n=3$; $l=0$; $m=0$; $s=-1/2$ (*With maximum electron*)

Sol. It means $1s^2 2s^2 2p^6 3s^2$

Hence total no. of electrons $=12=$ no. of protons $=$ Atomic No.

Hence (a) At. No. $=12$ (b) Probable atomic Mass $=24$

(Since all atoms except '*H*' have got at least same no. of neutrons as no. of protons)

(c) No. of electrons $=$ At. No. $=12$

19. *Write down the values of all the quantum number for the valency electrons of chlorine.*

Sol. Chlorine (Cl) $=$ At. No. $=17=1s^2$, $2s^2 2p^6$, $3s^2 3p_x^2 3p_y^2 3p_z^1$

V. E. $= 3s^2 3p^5$

No. of V. E.	*n*	*l*	*m*	*s*
$3s^1$ (e_1)	3	0	0	$+\frac{1}{2}$
$3s^2$ (e_2)	3	0	0	$-\frac{1}{2}$
$3p_x^1$ (e_3)	3	1	+1	$+\frac{1}{2}$
$3p_y^1$ (e_4)	3	1	0	$+\frac{1}{2}$
$3p_z^1$ (e_5)	3	1	−1	$+\frac{1}{2}$
$3p_x^1$ (e_6)	3	1	+1	$-\frac{1}{2}$
$3p_y^1$ (e_7)	3	1	0	$-\frac{1}{2}$

20. *Explain why half-filled and completely filled orbitals have extra stability.* **(AISB 1980)**

Ans. The electrons can exchange their positions at random in various orbitals of the same sub-shell. Due to this exchanging position of electrons the energy is generated which is called the **exchange energy**. As the exchange energy is maximum in the case of half-filled and completely filled orbitals therefore it results in the extra stability of these orbitals.

It has been seen that less repulsion is encountered between electrons having parallel spin (because they occupy different orbits). Two electrons with parallel spins will be associated with less energy in comparision to a random orientation of spins. This stabilisation energy is known as the exchange energy *K*. The total exchange energy stabilisation of a state is equal to the product of (i) the exchange energy per pair of parallel spin electrons and (ii) the number of distinct pairs of electrons with parallel spin which occupy a degenerate orbit (having the same energy state). The more the electrons with parallel spin, more the distinet pairs we can make by exchanging electrons.

Ex. *Cr* (At. No. 24) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^2$ **(Wrong)**
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ **(Correct)**
Cu (At. No. 29) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$ **(Wrong)**
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ **(Correct)**

21. *Write down the different orbitals for value of following quantum numbers :*

(i) $n=2,\ l=1,$
(ii) $n=3,\ l=2,$
(iii) $n=4,\ l=3,$
(iv) $n=1,\ l=0,\ m=0,$
(v) $n=2,\ l=1,\ m=-1,$
(vi) $n=3,\ l=1,\ m=+1$

Sol. (i) $2p$, (ii) $3d$, (iii) $4f$, (iv) $1s$, (v) $2p_z$, (vi) $3p_x$.

22. *The nucleus of an element contains* 11 *protons and* 12 *neutrons. What would be its atomic structure. Name the element.*

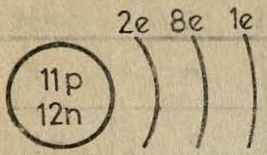


Fig. 1.19

Sol. Atomic number = no. of protons = 11 = No. of electrons.

Atomic mass = no. of protons + No. of neutrons = 11 + 12 = 23

Arrangement of electrons = 2, 8, 1

Hence the element is sodium (*Na*)

23. *A neutral element M has got the electronic configuration 2K, 8L, 5M. Find out the following :*

(*i*) *Atomic number* (*ii*) *probable atomic mass* (*iii*) *orbital wise configuration,* (*iv*) *total no. of electrons on p-sub-shell,* (*v*) *total no. of unpaired electrons,* (*vi*) *formula of hydride,* (*vii*) *formula of oxides,* (*viii*) *name of the element.*

Sol. $2K$ means there are 2 electrons on K-orbit ($1s^2$)
$8L$ means there are 8 electrons on L-orbit ($2s^2 2p^6$)
$5M$ means there are 5 electrons on M-orbit ($3s^2 3p^3$)

(i) Thus total no. of electrons $= 2+8+5 = 15$
$=$ No. of protons $=$ atomic number.

(ii) It should contain at least 15 neutrons
Hence probable atomic mass $= 15+15 = 30$

(iii) $1s^2,\ \ 2s^2 2p_x^2 p_y^2 p_z^2\ \ 3s^2 3p_x^1 p_y^1 p_z^1$

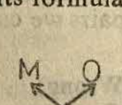
(iv) Total no. of electrons on p-subshell $= 6(2p^6) + 3(3p^3) = 9$

(v) Total no. of unpaired electrons $= 3$ i.e. $3p^3$

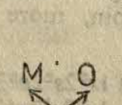
(vi) Formula of hydride is MH_3. It can not be MH_5 because the valency of the element with respect to hydrogen is never more than 4.

(vii) The valency of the element M, will be either 3 or 5.

Hence its formula will be



or M_2O_3;



or M_2O_5

(viii) Since the atomic no. $= 15$, hence the element is PHOSPHORUS.

24. *Given that the mass of the electron* $(m) = 9{\cdot}1 \times 10^{-31}$ *kg and* $h = 6{\cdot}627 \times 10^{-34}\ Js^{-1}$. *Calculate the wavelength of an electron moving with a velocity of* $4{\cdot}2 \times 10^4$ *m. s*$^{-1}$.

Sol. Mass of the electron $(m) = 9{\cdot}1 \times 10^{-31}$ kg.

Velocity of the electron $(v) = 4{\cdot}2 \times 10^4$ m. s^{-1}.

Planck's constant, $h = 6{\cdot}627 \times 10^{-34}$ Js

For calculating the wavelength, we use the relation.

$$\boxed{\lambda = \frac{h}{mv}}$$

$$\lambda = \frac{6{\cdot}627 \times 10^{-34}\ \text{Js}}{9{\cdot}1 \times 10^{-31}\ \text{kg} \times 4{\cdot}2 \times 10^{4}\ \text{ms}^{-1}}$$

$$= \frac{6{\cdot}627 \times 10^{-34}\ \text{kg m}^2\ \text{sec}^{-2}\ \text{sec}}{9{\cdot}1 \times 10^{-31}\ \text{kg} \times 4{\cdot}2 \times 10^{4}\text{ms}^{-1}}$$

$$= \frac{6{\cdot}627 \times 10^{-34}\ \text{kg m}^2\ \text{sec}^{-1}}{38{\cdot}22 \times 10^{-27}\ \text{kg ms}^{-1}} = 0{\cdot}173 \times 10^{-7}\ \text{m}$$

$$= 173\ \text{Å}$$

25. *Calculate the uncertainty in velocity* ($\triangle v$) *of an electron if the uncertainty in its position is* 2×10^{-10} *m.* ($h = 6{\cdot}627 \times 10^{-34}$ *Joule sec*)

Sol. Using Uncertainty Principle

$$\boxed{\triangle p \times \triangle x = m \triangle v \times \triangle x = \frac{h}{4\pi}}$$

Here $h = 6\ 627 \times 10^{-34}$ Joule sec

$m = 9{\cdot}1 \times 10^{-31}$ kg.

$\triangle x = 2 \times 10^{-10}$ m.

$$\triangle v = \frac{h}{4\pi m \triangle x}$$

$$= \frac{6{\cdot}627 \times 10^{-34}}{4 \times 3{\cdot}1416 \times 9{\cdot}1 \times 10^{-31} \times 2 \times 10^{10}}$$

$$= 2{\cdot}885 \times 10^{5}\ \text{cm sec}^{-1}$$

Thus for a 2 angstrom uncertainty in position, the uncertainty in velocity is a huge amount.

26. *An oxide of nitrogen has a molecular weight* 30. *The total number of electrons in one molecule of the compound* (*At. No.* $N = 7$, $O = 8$) *is*

(1) 14 (2) 15 (3) 16 (4) 7 (5) 18

Sol. Mol. wt. of the compound = 30. The oxide would thus be *NO* At. No. of electron in *M* and *O* being 7 and 8, the total number of electrons present in one molecule = 7 + 8 = 15. Hence (2) is correct.

27. *For elements* (*a*), (*b*), (*c*) *and* (*d*) *have the following electronic configurations respectively. Spot the least chemically reactive element among these.*

(1) 2, 8, 1 (2) 2, 8, 7 (3) 2, 4 (4) 2, 8 **[Varanasi 1975]**

Sol. The least chemically reactive elements are those which have 8 electrons in the outermost orbit.

Hence (4) is correct.

28. *Calculate the wave length and frequency of the radiation emitted in case of hydrogen atom when an electron jumps from third orbit to first orbit. Name the region of electromagnetic radiation in which this line will fall.* **[Roorkee 1985]**

Sol. Let the wavelength of radiation emitted is $\lambda = ?$
The frequency of radiation emitted is orbit $\nu = ?$
Number of higher orbit $n_2 = 3$
Number of lower orbit $n_1 = 1$.
Velocity of light $= 3 \times 10^{10}$ cm sec^{-1}

(i) To Calculate the Frequency of Radiation :

We know that $$\nu = \frac{2\pi^2 mZe^4}{h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad \ldots (1)$$

have $\pi = 3{\cdot}1416$, $m =$ mass of electron $= 9{\cdot}1 \times 10^{-28}$ gm $n_1 = 1$ $Z = 1$ for hydrogen, $e = 4{\cdot}8 \times 10^{-10}$ esu, $h = 6{\cdot}627 \times 10^{-27}$ erg sec. $n_2 = 3$ then upon substitution in equtation (1)

$$\nu = \frac{2 \times (3{\cdot}1416)^2 \times 9{\cdot}1 \times 10^{-28} \times (4{\cdot}8 \times 10^{-10})^4}{(6{\cdot}627 \times 10^{-27})^3}\left[\frac{1}{1^2} - \frac{1}{3^2}\right] \text{sec}^{-1}$$

$$= 3{\cdot}289 \times 10^{15}\left(1 - \tfrac{1}{9}\right) \text{sec}^{-1}$$

$$= 3{\cdot}289 \times 10^{15} \times \tfrac{8}{9} \text{ sec} \qquad \therefore \quad \nu = 2{\cdot}923 \times 10^{15} \text{ sec}^{-1}$$

(ii) To calculate the wavelength of the radiation

We know $$\lambda = \frac{c}{\nu} \quad \ldots (2)$$

Putting the values of c and ν in eqn. (2) we get

$$= \frac{3 \times 10^{10} \text{ cm sec}^{-1}}{2{\cdot}923 \times 10^{15} \text{ sec}^{-1}} = 1{\cdot}026 \times 10^{-5} \text{ cm.}$$

$$= 1026 \times 10^{-8} \text{ cm} = 1026 \text{ Å}$$

Since the wave length of radiation emitted is less than 3800 Å, the region of electromagnetic radiation in which the line falls is **ultra-violet**

29. *Calculate the energy difference between Bohr's first orbit and second orbit of hydrogen atom. Given*

R (Rydbergs constant) $= 109737$ *cm*$^{-1}$; $c = 3 \times 10^{10}$ *cm sec*$^{-1}$ *and* $h = 6{\cdot}627 \times 10^{-27}$ *erg-sec.*

Sol. Let the energy of the 2nd orbit $= E_2$
Let the energy of the first orbit $= E_1$

Difference of energy $= E_2 - E_1 = ??$
for first orbit $n_1 = 1$, for second orbit $n_2 = 2$

We known, $E_2 - E_1 = h\nu = hc\bar{\nu}$ $\left(\because \nu = \frac{c}{\lambda} = c\bar{\nu}\right)$

$\bar{\nu}$ = wave number

$$= hcR\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \left[\because \bar{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\right.$$

Vide equation (1-5)]

Putting the values of h, c, R, n_1 and n_2 in above equation, we have

$$E_2 - E_1 = 6{\cdot}627 \times 10^{-27} \text{ erg. sec} \times 3 \times 10^{10} \text{ cm sec}^{-1}$$
$$\times 109737 \text{ cm}^{-1}\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$
$$= 6{\cdot}627 \times 10^{-27} \times 3 \times 10^{10} \times 109737 \times \tfrac{8}{4} \text{ ergs}$$
$$= 1{\cdot}6345 \times 10^{-11} \text{ ergs} \qquad [1 \text{ J} = 10^7 \text{ erg}]$$
$$= 1{\cdot}6345 \times 10^{-18} \text{ Joules.} \qquad [\because 1 \text{ erg} = 10^{-7} \text{ J}]$$

According to Bohr, the energy E of an electron in any orbit is given by the expression :

$$E_n = -\frac{2\pi^2 m Z^2 e^4}{n^2 h^2}$$

where n is a whole number.

30. *Find out the expression for energy of H atom, He*$^+$*, Li*$^{2+}$ *and Be*$^{3+}$ *ion*

($h = 6{\cdot}627 \times 10^{-27}$ erg-sec; $e = 4{\cdot}8 \times 10^{-10}$ esu)

Sol. The energy E of an electron in any orbit is given by the relation,

$$E = -\frac{2\pi^2 m e^4 Z^2}{n^2 h^2} \qquad \ldots (1)$$

(i) Expression for energy of *He* atom. :
for *H* atom, $Z = 1$
Putting the value of $Z = 1$ in (1), we get

$$E_{\text{H}} = -\frac{2\pi^2 m e^4 . 1^2}{n^2 h^2} = -\frac{2\pi^2 m e^4}{n^2 h^2} \qquad \ldots (2)$$

(ii) Expression for energy of *He*$^+$ ion
For *He* atom, $Z = 2$
Putting the value of Z = 2 in (1), we get

$$E_{\text{He}^+} = -\frac{2\pi^2 m e^4 (1)^2}{n^2 h^2} = -\frac{8\pi^2 m e^4}{n^2 h^2} \qquad \ldots (3)$$

(iii) Expression for energy of Li^{2+} ion.

for Li = atom, $Z=3$

Putting the value of $Z=3$ in (1) we get

$$E_{Li^{2+}} = -\frac{2\pi^2 me^4(3)^2}{n^2h^2} = -\frac{18\pi^2 me^4}{n^2h^2} \quad .. \quad (4)$$

(iv) Expression for energy of Be^{3+} ion

for Be atom, $Z=4$.

Putting the value of $Z=4$ in (1) we get

$$E_{Be^{3+}} = -\frac{2\pi^2 me^4(4)^2}{n^2h^2} = -\frac{32\pi^2 me^4}{n^2h^2} \quad .. \quad (5)$$

31. *What is the energy in Joules of a single photon of wavelength* 250×10^{-9} metre ? (Roorkee 1984)

Sol. We know that :

$$E = h\nu = h\,\frac{c}{\lambda}.$$

Here h = Planck's constant $= 6{\cdot}627\times10^{-27}$ erg sec.
$= 6{\cdot}627\times10^{-34}$ Joule sec.
c = velocity of light $= 3\times10^{10}$ cm sec^{-1} $= 3\times10^{8}$ metre sec^{-1}
$\lambda = 250\times10^{-9}$ metre (by question)

Upon substitution these values in above equation

$$E = \frac{6{\cdot}627\times10^{-34}\text{ joules sec. } 3\times10^{8}\text{ metre sec}^{-1}}{250\times10^{-9}\text{ metre}}$$

$$= \frac{6{\cdot}627\times3}{250}\times10^{-34+8+9}\text{ Joules} = \frac{6{\cdot}627\times3}{250}\times10^{-17}\text{ Joules}$$

$$= \frac{19{\cdot}881}{25}\times10^{-18}\text{ joule} = 0{\cdot}79524\times10^{-18}\text{ joule},$$

$$= 7.9524\times10^{-19}\text{ Joule.}$$

32. *A neutral atom of an element has two K, eight L, nine M and two N electron. Write the elecrtonic configuration of the element and find :* **(Roorkee 1984)**

1. *total number of s electrons*
2. *total number of d electrons.*

Hint. 2 K, 8 L, 9 M, 2 $N = 2+8+9+2 = 21$

At. No. = 21 Electronic configuration

$$\underbrace{1s^2}_{K}\ \underbrace{2s^2 2p^6}_{L}\ \underbrace{3s^2 3p^6 3d^1 4s^2}_{M}$$

1. Total no. of s electrons $= 2+2+2+2 = 8$
2. Total no. of d electrons $= 1$

Exercises

Long Type

1. Explain the importance of the following in the elucidation of atomic structure.

(a) Cathode rays, (b) Positive rays, (c) alpha particle scattering experiment.

2. Write down the sub-orbitwise electronic configuration of elements whose atomic numbers are (1) 20, (2), 25, (3) 29, (4) 35, (5) 47 **(B. I. E. C. 1985)**
3. What are quantum number ? What do you know about the principal quantum number ? Write down the values of different quantum number for the last electron of (a) Carbon, (b) Potassium.
4. What is Neil's Bohr' theory of siationary orbit ? Mention its limitations.
5. What do you mean by nuclear stability ? What is odd even rules for this ? Write down the electronic configuration of Fe^{+2}.
6. Write down the electronic configuration of the following in terms of *s, p, d* and *f.*

   (a) Cu^{+2}, (h) Co^{+2}, (c) Cr^{+3}, (d) Ni^{+2}.
7. What is Pauli's exclusion Principle ? Why the maximum number of electron in *M*-shell is 18 ? Explain on the basis of quantum number.
8. An element *X* has electronic configuration 2 *K* 8*L* 5*M*. Find out the following :

   (a) At. No, (2) Probable at. mass, (c) total no. of *p*-electrons, (d) Block, (e) V. E., (f) Penultimate electrons, (g) Formula of oxides, hydrides and chloride, (h) Name of the element.
9. Write notes on, (a) Pauli's exclusion Principle, (b) Aufbau's principle, (c) Hund's Rule. (d) Quantum number.
10. An element *A* has an atomic weight 40 and atomic number 20.
    (a) Write down its electronic configuration enumerating its number of *e*, *p* and *n*.
    (b) Will this element be *A* metal or a non-metal ? Why ?
    (c) How will it react with dilute *HCl* ? Write down the chemical equation.
    (d) Write down the electronic structure of another element of smaller atomic weight having similar properties of *A*.
    (e) Write down the electron dot structure of the chloride of *A*.
11. (a) Explain the following terms :
    Orbit, orbitals, principal quantum number. **(I S M 1985)**
    (b) What are the various quantum numbers of the valence electron of *Na* (11) ?
12. Calculate the radius of the first orbit of electron in an atom of hydrogen. **(I S M. '1985)**
13. Deduce the possible values of all four quantum numbers for the 19th electron of *Cr* and 21st electron of *Sc* and *p*-electron of *N*. **(Roorkee 1983)**
14. (a) Write a short account about Rutherford's Model of the atom. **(I M S 1981, '84)**
    (b) What was the objection to the Rutherford's model ? **(I M S 1981)**
    (c) How it was overcome by Niel's Bohr. **(I M S 1981)**
15. The atomic number of certain atom is 35.
    Determine number of electrons in each shell and sub-shell of the atom. Mention with reasons whether it is an electropositive or electronegative element. **(I M S 1984)**

16. Write down the values of all the azimuthal quantum number for the principal quantum number $n=2$. **(I M S 1985)**

17. Two elements X and Y have atomic number 17 and 26 respectively.

(a) Give their electronic configuration in terms of s, p, d orbitals. **(I M S 1982)**

(b) Write most probable valency of the element from the consideration of electronic configuration. **(I M S 1982)**

(c) Are the elements metal or non-metals ? **(I M S 1982)**

18. Write notes on :

(a) Pauli's exclusion principle, (b) Hund's Rule, (c) Aubau's principle.

19. (a) Define the term quantum number. How many quantum numbers has an electron in the atom ? Describe each one of them.

(b) Write down the values of all the azimnthal quantum number and magnetic quantum number for principal quantum number $n=2$.

20. (a) Give the number of protons, electron and the electronic configuration of the following atoms.

$Cr(24)$, $Cu(29)$, $Fe(26)$, $Zn(30)$, $Ar(18)$

(b) Write the atomic structure of Mg^{+2}, S^{-2}, N^{-3}.

(c) Write the electronic configuration of Cr^{+2} and Mn^{+4} and give the number of unpaired electrons present in each case.

(Atomic number : $Cr=24$, $Mn=25$) **(Roorkee 1986)**

(d) Give electron distribution in orbitals of the atoms of the following elements, Nitrogen, Sodium, Chlorine and Calcium.

21. (a) Write down the electronic configuration of elements with atomic no. 24, 26, 29,. Indicate the block, group and period in which they are likely to be placed.

(b) Write down the values of all the quantum number for the valency electron of sulphur.

Short Type

22 An element has got one neutron more than proton. Its mass number is 39. Find out the number of neutrons and protons.

23. Write the names of three elementary particles of matter. Draw simplified diagrams of the atomic structure of nitrogen, sulphur and magnesium.

24. Draw the atomic structure of chlorine.

25. The atomic number of an element is 35 and atomic weight of two of its isotopes are 79 and 81. Find out :

(a) The number of electrons in the outermost orbit. (b) Valency of the element. (c) The number of neutrons and protons in the nuclei of the two isotopes.

26. If the electronic configuration of neon eaving atomic number 10 can be written as $15^2 25^3 2p^6$. Write electronic configuration of the elements A, B, C, having atomic number 17, 18 and 19 respectively and indicate which one of them is an alkali and which one is an inert element and why ? **(I. S. C. 1980)**

[Hints : Alkali metal $=C$**, Reason :** It contains one electron in its outermost orbit.]

Inert element $= B$, **Reason** : It possessess 8 electrons in the outermost orbit. A—Halogen.

27. Write down the name of three fundamental particles indicating their absolute mass in kg and charge in coulomb.

28. Given the atomic number of e lement which of the following can you find and which not ?

(a) The number of electrons in the atom, (b) The atomic weight, (c) The no. of isotopes, (d) The total positive charges on the nucleus, (e) The number of neutrons in the nucleus and, (f) The number of protons in the nucleus.

[**Hint** : The following can not be known :—

(a) At. Wt., (b) no. of isotopes, (c) the no. of neutrons in the nucleus.]

29. (a) An atom of an element contains 13 electrons. Its nucleus has 14 neutrons. Find out the atomic number and the approximate atomic weight of the element. Indicate the arrangement of electrons. (b) An isoptope of the element in (a) has atomic weight two units higher. What will be the number of protons, neutrons and electrons in this isoptope ?

30. Write down the atomic structure of :

(a) Na^+, (d) Phosphorus and (c) S^{-2}.

31. Give the electronic configuration of the elements with atomic number 35, 36 and 37. Give their names and mention with reason which one of them is an inert gas, an electropositive element and an electronegative element ?

[**Hint : At. No. 35-Bromine,** electronegative. Since it gains electron to have stable electronic configuration.

At. No. 36. **Krypton** : Inert element. Since it contains stable eletronic configuration.

At. No. 37. **Rubedium** : Electro+ve. Since it looses one electron to have stable configuration.

32. What defects were there in the Rutherford's Atomic model ? How Neil's Bohr removed these defects in his own atomic model ?

33. What do you know about principal and Azimuthal quantum number.

34. How will you show that in the fourth orbit ($n=4$) the maximum number of electrons can be 32.

35. Give the names of the four quantum number of an atom indicating the significance of each.

36. Write down the values of all the quantum number for the valency electrons of chlorine.

37. The mass of an atom is less than the mass of the particles present in it. Give reasons.

38. The nucleus of Helium atom is made up of 2 protons and 2 neutrons but the atomic mass of Helium is less than the combined masses of these protons and neutrons. Give reasons for this mass defect.

39. Why negatively charged electrons does not fall on positively charged nucleus to destroy the structure of atom ?

40. What explanation was given by Yukawa for the stability of nucleus ?

41. Write the electronic configuration of elements with atomic number 19, 29, 36. **(Roorke 1979)**

42. Represent mathematically :

(i) Energy of one quantum of light.
(ii) Electrons angular momentum as postulated by Bohr.
(iii) Relationship between energy and mass.

43. With the help of Pauli's exclusion principle, find out the maximum number of electrons that can be filled in the electronic shell having principal quantum number three ($n=3$).

44. An element appears in period two (first short period) of the periodic table. The nucleus of its atom possess eight protons and eight neutrons. Calculate the

mass number. Write down the distribution of electrons in different shells and sub-shells. Indicate the group in the periodic table to which the element belongs. Name the element.

45. Show the distribution of electrons in different shells and sub-shells of the three elements *A*, *B* and *C*, having atomic number, 1, 11 and 17 respectively. Indicate the groups in the Periodic table to which *B* and *C* can be included.

46. The atomic number of the two elements *A* and *B* are 9 and 17 respectively. Show the distribution of electrons in different shells and sub-shells of the atoms of these two elements. In the weight of electronic structure, explain why the element *A* is a stronger oxidising agent than the element *B*.

[**Hint** : Both have seven electrons in their outermost orbit. Since element *A* is smaller than *B*. Hence *A* gains electrons more readily than *B*. Hence *A* is stronger oxidising agent than *B*.]

47. Give the electronic configuration of elements with atomic number 11, 18 and 26 and name which "class elements" they respsectively belong to.

48. Name the elements that correspond to each of the following electronic configuratians :

$1s^2 2s^2 2p^6 3s^2 3p^1$, (b) $1s^2 2s^2 2p^6 3s^2 3p^3$, (c) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$.

49. A neutral atom of an element has 2*K*, 8*L* and 3*M* electrons. Find out the following from this data :

(a) Atomic number, (b) Total no. of *s* electrons, (c) No. of protons in the nucleus, (d) Valency of the element, (e) Name of the element.

Fill in the blanks :

50. (a) Electrically positive, negative and neutral units in atomic structure are called......... and..........

(b) The nucleus of an atom consists of.........and.........while the molecule consists of.........

(c) An element having atomic number 8 and mass number 16 is.........

(d) The isotopes of an element differ to the number of.........

51. Complete the following table for two naturally occuring isotopes both of element—

At. Mass.	*At. No.*	*No. of Protons*	*No. of Neutrons*	*No. of electrons*	*Charge on nucleus*
12				6	
13					

52. Fill in the blanks :

(i) The maximum number of electrons on any orbit is ....

(ii) The atomic number of the element having maximum number of unpaired 3*p* electrons is ....

(iii) The value of principal and azimuthal quantum number for the last electron of carbon is......... and..........

(iv) If *n*=3 then *l* Can have values from.........to.........

(v) The number of unpaired electrons in the ground and excited state of carbon is......... and.........

53. State whether the following statements are True or False.

(i) The energy of orbits decreased with increase in the value of *n*.

(ii) The neutron was discovered by J. J. Thomson.

(iii) The number of unpaired electrons in oxygen is 2.
(iv) The shape of an orbital is given by azimuthal quantum number.
(v) Copper is a *d*-block element.
(vi) An electron radiates energy spontaneously while in stationary orbit of an electron.
(vii) The electron density on the XY plane in $3d_{x^2-y^2}$ orbital is zero. **(IIT. 1986)**
(viii) The number of electrons on penultimate orbit of iron is 8.
(ix) The value of magnetic quantum number for the last electron of chlorine is zero.
(x) The maximum number of orbital in an atom is n^2.

54. Match the Column A With B.

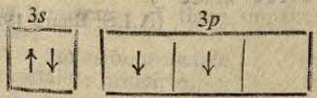
A	B
1. J. J. Thomson	a. Neutron
2. Moseley	b. Nucleus
3. Rutherford	c. Elliptical orbit
4. Chadwick	d. Spin Multiplicity
5. Niels Bohr	e Electron
6. Sommerfeld	f. Atomic number
7. Pauli	g Stationary orbit
8. Hund's rule	h. Exclusion Principle.

55. Complete the sentence in A with B.

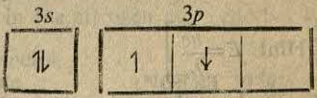
A	B
1. Proton was discovered by	(a) 18
2. The maximum number of electrons in *M*-shell will be	(b) 10
3. The maximum number of electrons on *d*-sub-shell will be	(c) Goldestin
4. The value of magnetic quantum number for the last electron of carbon will be	(d) 0, 1
5. The value of magnetic quantum number for the last electron of sodium will be	(e) 0
6. The value of *l* if $n=2$ will be	

Very Short Type

56. Give reason why the ground state outermost electronic configuration of Silicon is



and not



(IT 1985)

57. What is the maximum number of electrons that may be present in all the atomic orbitals with principal quantum number 3 and azimuthal quantum number 2 ? **(IIT 1985)**

58. Write down the values of azimuthal quantum number when $n=2$.

59. Write down the value of principal and azimuthal quantum number for the last electron of

(a) *Na* (b) *C* (c) *Fe*.

60. Atomic number of an element is 19 and its mass number is 39. Find out the number of neutrons in the nucleus.

61. Write down the dimension of radii of nucleus and the atom.

62. The charge on the electron is $1{\cdot}602 \times 10^{-19}$ coulombs. Its e/m value is $1{\cdot}759 \times 10^{8}$ coulombs/gm. Find the rest mass of the electron.

[Hint : Rest mass of electron $(m) = \frac{e}{e/m}$]

63. The atomic number of an element is 21. Determine the number of electrons in each shell and sub-shell of the atom.

64. The atomic number of an element is 29. Write down the electronic configruation in terms of *s*, *p* and *d*.

65. Give the values of magnetic quantum number (m) for azimuthal quantum number, $l = 3$.

66. Write down the quantum of all the electrons present in the outermost orbit of Argon ($A = 18$) **(Roorkee 1985)**

67. Give the mass of an electron in *kg*.

68. The electronic configuration of Helium is $1s^2$.
Write down the electronic configuration of, (a) Oxygen, (b) Sodium.

69. State the number of protons, neutrons and electrons in (i) ^{12}C, (ii) ^{14}C. Give their electronic configuration. **(IIS 1977, Gr A)**

70. How many electrons can reside in *s*, *p*, *d* and *f* orbitals.

71. What is the maximum number of electrons that can be filled in *M*-shell.

72. The mass number of three elements is 40 but their atomic number are 18, 19 and 20 respectively. How many protons and neutrons are presnt in thorm.

73. Write down the electronic configuration of the element having atomic number 9. **(AISB 1981)**

74. Two elements *X* and *Y* have atomic number 12 and 14 respectively, write down

(i) the electronic configuration of *X* and *Y*.
(ii) The group of periodic table to which they belong.
(iii) the prinicipal oxidation states.
(iv) the formula of their simplest chloride. **(I. Sc. 1980)**

75. Write down the electronic configuration of elements with atomic number 24 and 31 and on the basis of electronic configuration indicate the group of periodic table to which each element belong. **(Roorkee 1980)**

NUMERICALS

76. Calculate and compare the energies of two radiations which have length 6000 Å and 4000 Å ($h = 6{\cdot}6 \times 10^{-34}$ joule sec, $c = 3 \times 10^{8}\ m\ \text{sec}^{-1}$) **(A.I.S. Board 1982)**

$\left[\textbf{Hint. } E = \frac{hc}{\lambda}\right]$

77. Find out the total number of electrons in :

(a) One molecule, (b) one mole of a saturated hydrocarbon whose molecular weight is 30.

78. An oxide of nitrogen has molecular weight 92. Find out the total no. of electrons in one mole of oxide of nitrogen. **(CEE 1979)**

79. Calculate the energy difference between Bohr's first orbit and second orbit of hydrogen atom ($R=109737$ cm^{-1}, $c=3\times10^{10}$ cm. sec.$^{-1}$ and $h=6{\cdot}627\times10^{-27}$ erg. sec)

81. Calculate the energy emitted by excited hydrogen atom which gives a spectral line with values of n_1 and n_2 equal to 3 and 5 respectively.

82. What will be minimum uncertainty in the position of an electron when the uncertainty in the momentum is 1×10^{-4} gm cm sec^{-1}. ($h=6{\cdot}627\times10^{-27}$ erg/sec

[**Hint.** $\Delta x\times\Delta p=\frac{h}{2\pi}$; $p=1\times10^{-4}$ gm cm sec^{-1}]

83. Calculate the wave length associated with an electron (mass $9{\cdot}1\times10^{-31}$ kg) moving with a velocity of 10^3 m/sec. ($h=6{\cdot}6\times10^{-34}$ kg m^2 sec^{-1}) **(AISB 1983)**

84. Calculate the uncertainty in position of an electron of the uncertainty in its velocity is $5{\cdot}7\times10^5$ m/sec. ($h=6{\cdot}6\times10^{-34}$ kg m^2 sec^{-1}, mass of an electron$=9{\cdot}1\times10^{-31}$ kg) **(DSB 1982)**

85. Calculate the momentum of a particle which has a de Broglie wave length of 10^{-10} metre. ($h=6{\cdot}6\times10^{-34}$ kg m^2 sec^{-1}) **(AISB 1981)**

(b) What is the mass of a photon of sodium light ?

($\lambda=5894\mathring{A}=5{\cdot}894\times10^{-7}$ meters, $v=3\times10^8$ metre sec^{-1}. $h=6{\cdot}6\times10^{-72}$ kg m^2 sec^{-1}

Select and write correct answer for the following

86. According to Rutherford, nucleus of the atom consists of (a) Protons and neutrons, (b) protons and electrons, (c) Neutrons and protons, (d) protons only, (e) neutrons only.

87. Atomic number is related to :
(a) number of proton, (b) number of neutron, (c) number of α-particles. **(B.I.E.C. 1984)**

88 The ratio of the energy of a photon of 2000 Å wave length radiation to that of 4000 Å radiation is
(a) 1/4 (b) 4 (c) 1/2 (d) 2 **(IIT 1986)**

89. Which of the following sets of quantum numbers represent as impossible arrangement ?

	n	l	m_l	m_s
(a)	3	2	-2	1/2
(b)	4	0	0	1/2
(c)	3	2	-3	1/2
(d)	5	3	0	$-1/2$

(IIT 1986)

90. Sodium atom differs from sodium ion in the number of :
(a) protons, (b) neutrons, (c) electrons, (d) protons and electrons. **(NCERT 1974)**

91. The uncertainty principl was enunciated by
(a) Einstein, (b) Heisenberg, (c) Rutherford, (d) Pauli. **(NCERT' 1975)**

92. The preference of three unpaired electrons in the nitrogen atom can be explained by,
(a) Paul's exclusion principle, (b) Aufbau principle,
(c) Uncertainty principle, (d) Hund's rule. **(NCERT 1979)**

93. Cathode rays contain
(a) Electrons, (b) Protons, (c) Neutrons, (d) Atoms. **(BIEC 1985)**

94. Rutherford's alpha particle scattering experiment led to the conclusion that

(a) mass and energy are retated
(b) electrons occupy space around the nucleus

(c) neutrons are buried deep in the nucleus

(d) the point of impact with matter can be precisely determined. (IIT 1986)

95. Bohr Model can explain

(a) the spectrum of H-atom only,

(c) the spectrum of an atom or ion containing one electron only

(c) the spectrum of hydrogen molecule

(d) the solar spectrum.

96. The nucleus of an atom is made up of X protons and neutrons, for the most stable and abundant nuclei

(a) X and Y are both even, (b) X and Y are both odd,

(c) X is even and Y is odd, (d) X is odd and Y is even. (NCERT 1980)

97. Electromagnetic Radiation with maximum wave length is

(a) UV, (b) Radio wave, (c) X-ray, (d) IR. (IIT-1985)

98. When atoms are bomdarded with α-particles only a few in a million of the particles suffer deflections while others pass through undeflected. This is because :

(a) The force of attraction on the α-particles charged electrons is not sufficient.

(b) The nucleus occupies much smaller volume compared to the volume of atom.

(c) The force of repulsion on the fast moving electrons is small.

(d) The neutrons in the nucleus do not have any effect on the-particles. (NCERT 1980)

99. Neutrino has

(a) charge+1, mass 0 (b) charge 0, mass 0

(b) charge−1, mass 1, (d) charge 0, mass 1. (NCERT 1981)

100. $2p$ orbital have :

(n) $n=1$. $l=2$, (b) $n=1, l=0$, (c) $n=2, l=1$, (d) $n=2, l=0$ (NCERT 1981)

101. The quantum number that specifies the orientation of an atomic orbital in space is :

(a) the principal quantum number, (b) Azimuthal quantum number.

(c) Spin quantum number. (d) Magnetic quantum number. (NCERT 1982)

102. A metal M with atomic mass 27 has 14 neutrons in the nucleus of its atom. The element belongs to

(a) 1st group, (b) 2nd group, (c) 3rd group, (d) 4th group.

103. Correct set of four quantum numbers for the valence (outermost) electron of rubidium ($Z=37$) is:

(a) $5, 0, 0, +\frac{1}{2}$, (b) $5, 1, 0+\frac{1}{2}$

(c) $5, 1, 1, +\frac{1}{2}$, (d) $6, 0, 0, +\frac{1}{2}$. (IIT 1984)

104. The increasing order (lowest first) for the values of e/m (charge/mass) for electron (e), proton (p), neutron (n) and alpha participle (α) is

(a) e, p, n, α, (b) $n, p. e, \alpha$,

(c) n, p, α, e, (d) n, α, p, e. (I.I.T. 1984)

105. The azimuthal quantum number of the 17th electron of chlorine atom is :

(a) one, (b) two, (c) three, and (d) zero. (B. I. E. C. 1984)

106. The number of protons present in the nucleus of an atom is equal to its

(a) Mass number, (b) Atomic number, (c) Atomic weight. (B. I. E. C. '1985)

* * *

CHAPTER 2

RADIOACTIVITY

2.1. Introduction :

Radioactivity was discovered by Henry Becquerel in 1896. He found that crystals of Potassium uranyl sulphate possess certain peculier properties. The photographic plates placed near this salt in the dark were affected, indicating that some invisible penetrating radiations similar to that of X-rays are continuously emitted from this substance. He subsequently found that not only potassium uranyl sulphate but also other uranium salts possess the same property. The rays emitted by such substances are able to (i) ionize gases (ii) penetrate through thin metal sheets and (iii) produce luminosity in zinc sulphide. Substances which emits such active rays were called *radioactive* and the phenomenon was known as *radioactivity* :

Later on, Madam Curie (1902) found that pitchblende, an uranium mineral was far more radioactive than equal amount of uranium itself. This led her to conclude the presence of some highly radioactive elements in the mineral. Her prolonged efforts in separation resulted in the discovery of the element Radium which possesses radioactivity several million times to that of uranium. At present over 40 natural radioactive elements are known.

The radioactive radiation emitted by these elements are found to consist of the following—

(i) α—(alpha) particles (ii) β—(beta) particles (iii) γ—(gamma) or photons.

Definition : *The phenomenon of spontaneons emission of powerful radiations exhibited by certain unstable nucleus is called radioactivity.*

2.2. General Properties.

(1) The radiations emitted by radioactive substance are found to possess (i) high penetrating power, (ii) affect photographic plates, (iii) ionise gases, (iv) cause scintillations on fluorescent screens, (v) develop heat and (vi) produce chemical effects.

(2) As the radiations are given out, new elements are formed in an irreversible process, each element having its own characteristic radiations.

(3) The emission of radiations is spontaneous and is uneffected by any external agencies (temperature, pressure, chemical combinations etc.)

(4) The emission is not instantaneous but prolonged i. e. delayed action, extended over a certain period of time, otherwise it can not have been discovered at all.

2.3. Nature of Radioactive Rays

The rays emitted from such substances were later shown to be heterogeneous in character. Their composite nature was investigated by Rutherford (1902) who subjected these rays to an electric field and magnetic field and found to consist of three types of radiations α, β and γ-rays. These rays bending towards the negative plate is shown to consist of positively charged particles which he called α-particles. Those bending towards the positive plate were found to consist of negatively charged particle which were called β-particles. The rays going undeflected being neutral in character is called γ rays.

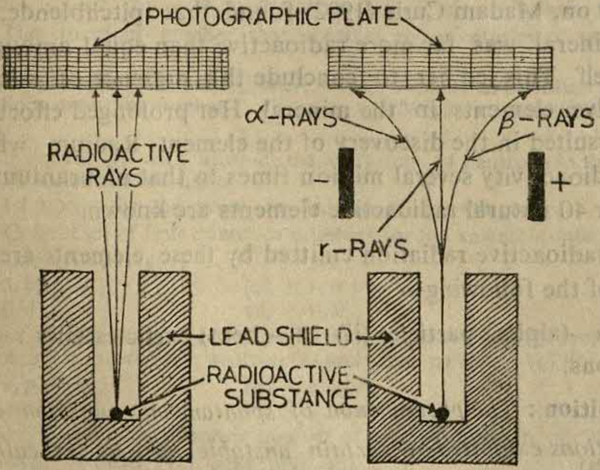


Fig. 2.1. Resolution of α, β and γ rays.

(**Please note :** αα, ββ and αβ cannot be emitted in a single step)

2.4. Comparative study of different types of radiations (α, β and γ rays)

S. N.	*Property*	*α-particles*	*β-particles*	*γ-rays*
1.	origin and occurrence	From the nucleus due to different energy levels in the nucleus	Mainly from the nucleus by conversion of neutrons to protons $^1_0n \rightarrow {^1_1p} + {_{-1}^{\ 0}e} + \overline{\nu}$ $\downarrow$ $\quad\downarrow$ Life 12·8 minutes $\quad$ anti-nutrino	Mainly from the nucleus during emission of α- and β-particles
2.	Nature	positively charged	negatively charged	neutral
3.	Charge in coulomb	$3{\cdot}2 \times 10^{-19}$	$-1{\cdot}6 \times 10^{-19}$	zero
4.	Structure	Doubly charged helium atom i.e., 2*p* and 2*n*.	Fast moving electrons	Electromagnetic rediation having wavleength in the range of 10^{-13} metre
5.	Rest mass in kg	$6{\cdot}444 \times 10^{-27}$	$9{\cdot}11 \times 10^{-31}$	zero
6.	*e*/*m* in coulomb/kg	$4{\cdot}8 \times 10^{7}$	$1{\cdot}75 \times 10^{11}$	zero/zero
7.	Velocity in metre per second	Varies from $1{\cdot}4 \times 10^{7}$ to $2{\cdot}3 \times 10^{7}$ (from socurce to source)	1×10^{8} to $2{\cdot}97 \times 10^{8}$	3×10^{8}
8.	Ionising power	strongest $\alpha = 10^{2}\ \beta = 10^{4}\ \gamma$	$\beta = \frac{1}{100}\ \alpha = 10^{2}\gamma$	$\gamma = \frac{1}{10^{4}}\ \alpha = \frac{1}{100}\ \beta$

S.N.	*Property*	*α-particles*	*β-particles*	*γ-rays*
9.	Penetrating power	Weakest $\alpha=\frac{1}{100}\,\beta=\frac{1}{10^4}\,\gamma$	$\beta=10^2\alpha=\frac{1}{100}\,\gamma$	$\gamma=10^2\beta=10^4\alpha$
10.	Fluorescence	Shown when they fall on certain substances	Shown when they fall on certain substances	Shown when they fall on certain substances.
11.	Scattering	Scattered while passing through thin metal sheets	More readily scattered by atomic nuclei	Scattering by crystals in the same way as *X*-rays
12.	Effect of electric and magnetic fields	Can be deflected by both	Can be deflected by both	Not deflected
13.	Effect on photographic plates	Can affect photographic plate	Can affect photographic plate	Very strong actions on photographic plate.
14.	Range i.e., the distance after which ionisation ceases	Can penetrate about 5 cm in air	Can penetrate about 5 mm *Al* or 1 mm of *Pb*.	Can penetrate about 30 cm of *Fe*
15.	Exposure to human body	Long exposure causes incurable burn	Harmful effect	Strong action on biological tissues used in Radium therapy for treatrnent of cancer, tumers.
16.	Energy in *MeV*	8 to 10	0·9 to 1·1	1·2 or slightly greater.

2.5. Difference between Radioactive Change and Chemical Change

Radioactive Change	*Chemical Change*
1. There is a change in the atomic number of concerned atoms.	1. There is no change in atomic number of the concerned atoms.
2. It does not depend upon external factors like temperature and pressure.	2. It depends much on external factors.
3. It does not depend upon chemical composition.	3. It depends completely upon the chemical composition.
4. It is an irreversible process.	4. It may be a reversible.
5. It involves large energy change (about 10 times of a chemical change).	5. It involves comparatively very low energy change
6. It involves nuclear transformations of the atoms concerned.	6. It involves outer electrons of the reacting atoms.
7. It is a first order process.	7. It may be zero, first or higher order process.

2.6. Radioactive Changes

Radioactive elements undergo two types of changes. The change which occurs as a result of the emission of alpha-particle is called *alpha-particle change* and that by the emission of a beta-particle is called a *beta-particle change*. They are discussed below :

2.7. Alpha-Particle Change

When an α-particle (He^{++}) is ejected from the nucleus, four units of mass number and two units of positive charge are removed from it. The new atom will have mass numbers less by 4 and atomic number less by 2. The new atom so formed will occupy a place two columns to the left of the parent element e.g.

$$\text{Uranium } (U) \xrightarrow{-\alpha({}_{2}^{4}He)} \text{Thorium } (Th)$$

mass number 234; Atomic number 92 Group VI — mass number 230, Atomic number 90 Group IV

2.8. Beta-Particle Change

When a β-particle is ejected, the nucleus gains one positive charge with no change in mass number. Thus the new atom will have the atomic number greater by one from the parent atom but with no change in the atomic number. The new element will fall one column to the parent element in the Periodic table.

$$\text{Thorium } (Th) \xrightarrow{-\beta({}^{0}_{-1}e)} \text{Protactinium } (Pa)$$

mass number 234, Atomic number (90) Group IV — mass number· 234, Atomic number 91 Group V

2.9. Group Displacement Law

Radioactive element undergoes two types of changes (a) α-particle change and (b) β-particle change, which have been summed up in the form of Group Displacement Law of Faj an, Russels and Soddy as given below :

Law I. If a radioactive element loses an α-particle, the *daughter element has* 4 *atomic mass unit (a. m. u.) less and it is displaced two positions towards the left in the Periodic table as compared to the position of the parent element in the periodic table—*

Example : $${}^{238}_{92}U \longrightarrow {}^{234}_{90}Th + {}^{4}_{2}He \text{ (α-particle)}$$

(Parent element) (Original) — (Daughter element) (New)

↓

Mass number→4 unit less than the original.
Atomic number→2 unit less than the original.

Law II. But if a radioactive element loses a β-particle, *the daughter element has the same mass as that of the parent element and it moves one place ahead in the Periodic table as compared to the parent element.*

Example : $${}^{234}_{92}Th \longrightarrow {}^{231}_{91}Pa + {}^{0}_{-1}e \quad \text{(β-particle)}$$

Parent (original) — Daughter (New)

↓

Mass number→same as original
Atomic number→One unit more than the original.

Note : It may be pointed out that the emission of a β-particle results in the production of an **isobar**, whereas the emission of **one α-particle** followed by two **β-particle** separately i.e., (α+2β) results in the formation of an **isotope** of the parent element. This can be shown by the following examples

Example 1

$$ {}^{226}_{88}Ra \xrightarrow[\text{i.e., } -\alpha\text{-particle}]{-{}^{4}_{2}He} {}^{222}_{86}Rn \xrightarrow[\text{i.e., } -\beta\text{-particle}]{-({}^{0}_{-1}e)} $$

(A) (B)

$$ {}^{222}_{87}Fr \xrightarrow[\text{i.e., } -\beta\text{-particle}]{-({}^{0}_{-1}e)} {}^{222}_{88}Ra $$

(C) (D)

A and *D* are isotope i.e,. ${}^{226}_{88}Ra$ and ${}^{222}_{88}Ra$

B, *C* and *D* are isobar i.e., ${}^{222}_{86}Ra$, ${}^{222}_{87}Fr$ and ${}^{222}_{88}Ra$

Example 2

$$ {}^{238}_{92}U \xrightarrow[\text{i.e. } -\alpha\text{-particle}]{-({}^{4}_{-2}He)} {}^{234}_{90}Th \xrightarrow[\text{i.e. } -\beta\text{-particle}]{-({}^{0}_{-1}e)} $$

(A) (B)

$$ {}^{234}_{91}Pa \xrightarrow[\text{i.e. } -\beta\text{-particle}]{-({}^{0}_{-1}e)} {}^{234}_{92}U $$

(C) (D)

A and *D* are isotope i.e. ${}^{238}_{92}U$ and ${}^{234}_{92}U$

B, *C* and *D* are isobar i.e., ${}^{234}_{90}Th$, ${}^{234}_{91}Pa$ and ${}^{234}_{92}U$

2.10. Law of Radioactive Disintegration, Disintegration Rate and Disintgeration Constant

The radioactive disintegration is found to obey the following two laws.

(i) Atoms of all radioactive elements undergo spontaneous disintegration to form fresh radioactive products with the emission of α, β and γ-rays.

(ii) The rate of radioactive disintegration i.e. the number of disintegration per second, is not affected by invironmental factors (like temperature, pressure and chemical combination etc.) **but** depends on the number of atoms of the original kind present at any time.

2.11. Expression for Radioactive Decay

The decay of a radioactive element is a random process and is not influenced by external factors such as temperature, pressure etc. The rate of decay is direclty proportional to the number of atoms present, following an exponential law. The rate of decay decreases with time. **Kinetically the process is a first order reaction.** Consider a radioactive element A disintegrating to give the product.

$$A \longrightarrow \text{Product}$$

i.e., the rate of disintegration will be

$$-\frac{dN}{dt} \propto N \qquad .. \quad (2.1)$$

Rate of decay $$-\frac{dN}{dt} = \lambda N \qquad .. \quad (2.2)$$

Where dN is the number of atoms decaying during time dt, N = the number of radioactive atoms present,

t = the time and λ is the decay constant and its value depends on the decaying element.

Rearrangement of equation followed by integration of equation (2.2)

$$-\int \frac{dN}{N} = \lambda \int dt$$

or $$-\log_e N = \lambda t + \text{constant } (C) \qquad .. \quad (2.3)$$

Where "C" is the integration constant.

Initially $t = 0$, $N = N_0$, then from equation .. (2.3)

$$-\log_e N_0 = C \qquad .. \quad (2.4)$$

Substituting the value of C in equation (2.3),

We have,

$$-\log_e N = \lambda t - \log_e N_0$$

or $$\log_e \frac{N_0}{N} = \lambda t \qquad .. \quad (2.5)$$

or $$\log_e \frac{N}{N_0} = -\lambda t \qquad .. \quad (2.6)$$

or $$\frac{N}{N_0} = e^{-\lambda t} \quad \text{or,} \quad \boxed{N = N_0 e^{-\lambda t}} \qquad .. \quad (2.7)$$

Which is graphically represented as shown in fig. 2.2.

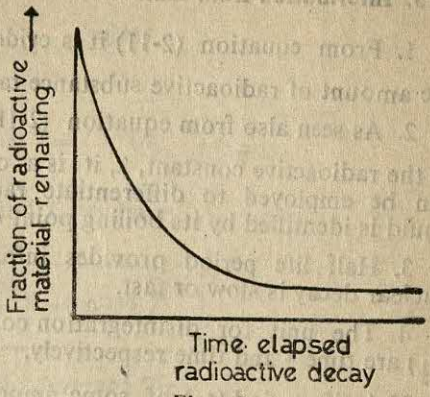


Fig. 2.2

[Conversion of Napierian logerithms to ordinary logerithms gives from equation (2−5)

$$2{\cdot}303\ \log_{10} \frac{N_0}{N} = \lambda t \quad .. \quad (2.8)$$

2.12. Half Life Period

The half life period of a radioactive element may be defined as the time during which a given amount of that radioactive substance is reduced by disintegration to half of its initial amount.

Let $t_{\frac{1}{2}}$ (Half life period) represent the time needed for the original activity to decrease to a half i.e., $N = \frac{1}{2} N_0$, then from equation (2-8)

$$.2{\cdot}303\ \log_{10}\left(\frac{N_0}{\frac{1}{2} N_0}\right) = \lambda t_{\frac{1}{2}} \quad .. \quad (2.9)$$

or

$$2{\cdot}303\ \log_{10} 2 = \lambda t_{\frac{1}{2}}$$

or

$$2{\cdot}303 \times 0{\cdot}30103 = \lambda t_{\frac{1}{2}} \quad .. \quad (2.10)$$

or

$$0{\cdot}6931 = \lambda t_{\frac{1}{2}} \text{ (as } \log_{10} 2 = 0{\cdot}30103)$$

$$\boxed{\therefore\ t_{\frac{1}{2}} = \frac{0{\cdot}6931}{\lambda}} \quad .. \quad (2.11)$$

Combining equations (2.8) and (2.10), we have

$$\frac{t}{t_{\frac{1}{2}}} = \frac{2{\cdot}303\ \log_{10} \frac{N_0}{N}}{2{\cdot}303\ \log_{10} 2} = \frac{\log_{10} \frac{N_0}{N}}{\log_{10} 2}$$

$$\boxed{\therefore\quad t = t_{\frac{1}{2}} \cdot \frac{\log_{10} \frac{N_0}{N}}{\log_{10} 2}} \quad .. \quad (2.12)$$

2.13. Information from Half life

1. From equation (2-11) it is evident that $t_{\frac{1}{2}}$ is independent of the amount of radioactive substance taken originally.

2. As seen also from equation (2-11) $t_{\frac{1}{2}}$ is inversely proportional to the radioactive constant, λ, it is a characteristic constant which can be employed to differentiate radioactive substances just as a liquid is identified by its boiling point or a solid by its density.

3. Half life period provides information whether a particular nuclear decay is slow or fast.

4. The unit for disintegration constant (λ) and half life period ($t_{\frac{1}{2}}$) are time^{-1} and time respectively.

Half life period ($t_{\frac{1}{2}}$) of some important radioactive element is tabulated.

TABLE

Name of Radioactive Elements.	*Half life period*	*Name of Radioactive element*	*Half life period*
$^{238}_{92}U$ (uranium)	$4{\cdot}51\times10^{9}$ years	$^{133}_{53}I$ (Iodine)	8·05 days
$^{226}_{88}Ra$ (Radium)	1590 years	$^{35}_{16}S$ (Sulfur)	87 days
$^{222}_{26}Rn$ (Radon)	3·82 days	$^{137}_{55}Cs$ (Cesium)	30 years
$^{216}_{84}Po$ (Polonium)	$1{\cdot}5\times10^{4}$ years	$^{60}_{27}Co$ (Cobalt)	5 years
$^{14}_{6}C$ (Carbon)	5760 year	$^{234}_{90}Th$ (Thorium)	$1{\cdot}4\times10^{10}$ years

Information from Above Table

From table, $t_{\frac{1}{2}}$ for $Ra = 1590$ yrs, if we take 10 gram of Ra today, 5 gm. of it will decay in 1590 years and after the end of this period only 5 gm. of Ra will be left.

2.14. Average Life Period (T)

The average life period of an individual radioactive element is equal to the reciprocal of the decay constant, mathematically,

$$\textit{Average life Period, } T = \frac{1}{\lambda} \qquad \text{.. (2.13)}$$

Now from equation (2.11) $t_{\frac{1}{2}}=\frac{0{\cdot}6931}{\lambda}$

and from equation (2.13) $T=\frac{1}{\lambda}$ or, $\lambda=\frac{1}{T}$

Combining two i.e., $t_{\frac{1}{2}}$ and T, we have

$$\boxed{t_{\frac{1}{2}}=\frac{0{\cdot}6931}{\lambda}=0{\cdot}6931\ T} \quad .. \quad (2.14)$$

Half life period $=0{\cdot}6931\times$ Average life

or Half life period 69·31% of average life.

2.15. Radioactive Series

A radioactive element disintegrates to produce a new element and this process of disintegration continues till an element incapable of further decay is obtained. Such a series of elements from the initial element to the end product is known as a *radioactive series.* There are four such series :

1. **Uranium series** ($4n+2$ **series**): This series begins with $^{238}_{92}U$ which has half life of $4{\cdot}5\times10^9$ years. The end product of this series is the stable isotope of lead ($^{206}_{82}Pb$). If the atomic weight of this Pb isotope (206) be divided by 4, the remainder is 2. Hence the series is called $(4n+2)$ series where n is an integer.

2. **Thorium series** ($4n$ **series**) : The starting element of this series is thorium (232) with a half life of $1{\cdot}39\times10^{10}$ years. The end product is lead (208). Likewise this series is called the $4n$ series since the atomic weight 208 is exactly divisible by 4.

(iii) **Actinium series** ($4n+3$ **series**) : The series starts with isotope of Uranium, $^{235}_{92}U$ of half life $7{\cdot}0\times10^8$ years. The end product is $^{207}_{82}Pb$ giving it the name of $(4n+3)$ series.

(iv) **Neptunium series** ($4n+1$ **series**) : This contain artificially synthesised trans—Uranium elements. Its starting member plutonium (241) has the longest half life of 13 years. No member of the series is found in nature.

The above series is tabulated below :

TABLE

Name of series.	Type :	*Name of isotope with (Parent nucleide)*	*Name of isotope end with.*	$t_{\frac{1}{2}}$ *of parent.*
Theorium	$4n$	$^{232}_{90}Th$	$^{208}_{82}Pb$	$1{\cdot}4\times10^{10}$ years
Neptunium	$4n+1$	$^{241}_{94}Np$	$^{209}_{83}Bi$	$2{\cdot}25\times10^{6}$ years
Uranium	$4n+2$	$^{238}_{92}U$	$^{206}_{82}Pb$	$4{\cdot}5\times10^{9}$ years
Actinium	$4n+3$	$^{235}_{92}U$	$^{207}_{82}Pb$	$7{\cdot}0\times10^{8}$ years.

2.16. Nucleon :

The particles such as proton, neutrons etc. present in the nucleus are called nucleons.

2.17. Measurement of Radioactivity :

The radioactivity can be measured by (1) Electroscopic method (2) Geiger-Muller (*G-M*) counter method.

218 Unit of Radioactivity :

(a) **Curie.** The unit for measuring radioactivity is curie. One curie is defined as that, quantity of radioactive material which gives $3{\cdot}7\times10^{10}$ disintegration per second. It was originally based on the rate of disintegration of 1 gram of radium.

1 curie (c) $= 3{\cdot}7\times10^{10}$ disintegration per second (*d. p. s.*)
1 millicurie ($1mc$) $= 3{\cdot}7\times10^{7}$ disintegration per second (*d. p. s.*)
1 Microcurie ($1\mu c$) $= 3{\cdot}7\times10^{4}$ disintegration per second (*d. p. s.*)

(b) **Rutherford :** A new absolute unit of radioactivity has recently been suggested. Its name is rutherford (*rd*). One rutherford is defined as quantity of a radioactivity substance which gives 10^6 disintegration per second.

(1 rutherford) $= 10^6$ d.p.s, (1 milli rutherford) $= 10^3$ d.p.s, (1 micro-rutherford) $= 1$ d.p.s.

(c) **Becquerel :** 1 Becquerel $= 1$ *d. p. s.*

2.19. Nuclear Reactions :

Nuclear reactions are transformation in atomic nuclei brought about by their interactions with elementary particles or with one another. According to Bohr's idea, the general scheme of nuclear reaction is

$$A+B\longrightarrow C\longrightarrow P+O$$

where A is a target nucleus
B is a projectiles
C is a compound nucleus

P is the residual product nucleus
O is an outgoing particle

2.20. Rules to be observed for writing a Nuclear Reaction :

In writing the nuclear reactions, remember the following rules.

(a) The sum of the mass number of initial particles (L. H. S.) should be equal to that of the mass number of product particles (R.H.S.)

(b) The sum of the atomic numbers of initial particles (L.H.S.) should be equal to that of the atomic number of product particles (R.H.S.)

(e) In all nuclear reactions, the total sum of mass and energy is conserved.

The particles which would be encounted in the nuclear reaction is tabulated as.

TABLE

Name of Particle	*Symbol*
Alpha	^4_2He
Beta or electron	$-^0_1 e$ or β^-
Positron	$+^0_1e$, or β^+
Gamma	$^0_0\gamma$ or γ
Proton	^1_1H or p
Neutron	^1_0n or n
Deutron.	^2_1H or ^2_1D or d

2.21. Rules to Balance a Nuclear Reaction :

The sum of the superscripts (mass numbers), written or implied must also be the same on the two sides of equation. The sum of the superscripts (Mass numbers), written, must also be the same on the two sides of the equation. Thus the equation for the primary radioactivity of $^{226}_{88}Ra$ is

$$^{226}_{88}Ra \longrightarrow ^{222}_{86}Rn + ^{4}_{2}He$$

Many nuclear processes may be indicated by a shorthand notation. The symbols $n, p, d, \alpha, \beta^{-}, \beta^{+}, \gamma$ are used to represent neutron, proton, deuteron ($^{2}_{1}H$), alpha, electron, positron and gamma rays, respectively. The atomic numbers are commonly omitted because the symbol for any element implies its atomic numbers. Examples of the corresponding long and shorthand notations for several reactions follow :

(a) $^{14}_{7}N + \underset{(p)}{^{1}_{1}H} \longrightarrow ^{11}_{6}C + \underset{(\alpha)}{^{4}_{2}He}$ $\quad ^{14}N(p, \alpha)^{11}C$

(b) $^{27}_{13}Al + \underset{(n)}{^{1}_{0}n} \longrightarrow ^{27}_{12}Mg + \underset{(p)}{^{1}_{1}H}$ $\quad ^{27}Al\,(n, p)^{27}Mg$

(c) $^{55}_{25}Mn + ^{2}_{1}H \longrightarrow ^{55}_{26}Fe + 2\,^{1}_{0}n$ $\quad ^{55}Mn(d, 2n)^{55}Fe$

2.21. Complete the following nuclear reactions

(a) $^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ?$

(b) $^{23}_{11}Na + ^{2}_{1}H \longrightarrow ^{20}_{10}Ne + ?$

(c) $^{7}_{3}Li + ?? \longrightarrow ^{4}_{2}He + ^{4}_{2}He$

(d) $^{238}_{92}U + ^{1}_{0}n \longrightarrow ??$

(e) $^{12}_{6}C + ^{1}_{1}H \longrightarrow ^{13}_{7}N + ?$

(f) $^{227}_{90}Th \longrightarrow ^{227}_{91}Pa + ?$

Sol. (a) $^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ?$

$$\text{In L. H. S.}\left\{\begin{array}{l}\text{Total Mass Number} = 14+1=15\\ \text{Total Atomic Number} = 7+0=7\end{array}\right.$$

$$\boxed{\text{In R. H. S.}}\left\{\begin{array}{l}\text{Total mass No.} = 14\\ \text{Total At. No.} = 6.\end{array}\right.$$

Deficiency in mass number $= 15 - 14 = 1$

Deficiency in at. number $= 7 - 6 = 1$

Hence it is represented by the symbol ${}^{1}_{1}H$

$$\therefore \quad {}^{14}_{7}N + {}^{1}_{0}n \longrightarrow {}^{14}_{6}C + {}^{1}_{1}H$$

It may also be represented as ${}^{14}_{7}N\ (n, p)$

(b) ${}^{23}_{11}Na \ + {}^{2}_{1}H \dashrightarrow {}^{21}_{10}Ne + \ ?$

As above, mass number difference $= (23+2) - (21) = 4$
Atomic number difference $= (11+1) - (10) = 2$

$\therefore$ Unknown particle $= {}^{4}_{2}He$ i.e. $\alpha-$particle.

$\therefore \ {}^{23}_{11}Na \ + \ {}^{2}_{1}H \longrightarrow {}^{21}_{10}Ne \ + \ {}^{4}_{2}He$ or ${}^{23}_{11}Na\ ({}^{2}_{1}d, \alpha)$

Similarly by above rule.

(c) $\therefore \ {}^{7}_{3}Li + {}^{1}_{1}H \longrightarrow {}^{4}_{2}He + {}^{4}_{2}He$ or, ${}^{7}_{3}Li(p, 2\alpha)$

(d) $\therefore \ {}^{238}_{92}U + {}^{1}_{0}n \longrightarrow {}^{239}_{92}U$ (neutron capture)

(e) $\therefore \ {}^{12}_{6}C + {}^{1}_{1}H \longrightarrow {}^{13}_{7}N + \gamma$ or ${}^{12}_{6}C\ (p, \gamma)$

(f) ${}^{227}_{90}Th \longrightarrow {}^{227}_{91}Pa + {}^{0}_{-1}e\ (\beta^{-})$

2.22. Mass Defect in Atomic Nuclei

With the developement of the mass spectrograph (an apparatus which measures mass number or atomic mass), it became possible to determine atomic mass with high degree of accuracy. It has been found that actual atomic mass of an element is invariably less the sum of the masses of proton, neutron and electron present in it. The difference between the two is known as **mass defect.** Obviously, the mass of the atom is equal to the sum of the masses of (i) Z (protons), (ii) Z (electrons), (iii) $(A—Z)$ neutron.

Let : A = mass number
Z = atomic number
$(A—Z)$ = number of neutrons
if m_p = mass of proton
m_n = mass of neutron
m_e = mass of electron

$\therefore$ The calculated mass of an atom should be given by

$$\begin{aligned} M &= Zm_p + Zm_e + (A-Z)m_n \\ &= Z(m_p + m_e) + (A-Z)m_n \\ &= Z(m_{\mathrm{H}}) + (A-Z)m_n \end{aligned} \qquad (\because \ \underset{\substack{\downarrow \\ \text{mass of hydrogen atom}}}{m_{\mathrm{H}}} = m_p + m_e)$$

Let A be the experimentally determined atomic mass (obtained from mass spectrograph) which is found to be less than M

The mass defect = Calculated mass − Atomic mass

$$= M - A = \Delta \text{ (say)}$$

$$\therefore \quad \Delta = [Z(m_H) + (A - Z\}m_n - A]$$

The mass number of some particle are given below in table :

TABLE

Mass of a proton = 1·00758 amu
Mass of a neutron = 1·00893 amu
Mass of an electron = 0·0005486 amu
Mass of α-particle = 4·00390 amu

Example : The Mass of the *He* is 4·00390 amu. (actual mass = A)

He contains 2 protons + 2 neutrons + 2 electrons.

Its mass should be

$$= \underset{\text{(mass of } 2\bar{e})}{(2 \times 0.005486)} + \underset{\text{(mass of 2 proton)}}{(2 \times 1{\cdot}00758)} + \underset{\text{(Mass of 2 neutron)}}{(2 \times 1{\cdot}00893)}$$

= 4·03411 expected mass = M)

The difference between the expected mass and the actual mass ie. Mass Defect = $M - A$

$$= 4{\cdot}03411 - 4{\cdot}00390 = 0{\cdot}03021 \text{ amu.}$$

For the highter elements the mass defect is negative and for the heavier ones it is positive.

2.23. Packing Fraction

The difference between the atomic mass and mass number is called **mass defect.** The ratio of the mass defect and the mass number is called the **packing fraction.** *Thus packing fraction is the divergence of the mass of any atom from the nearest whole number divided by the mass.*

$$\text{Packing Fraction } (f) = \frac{\text{isotopic mass} - \text{mass number}}{\text{mass number.}} \times 10^4$$

$$= \frac{M - A}{A} \times 10^4. = \frac{\text{Mass Defect}}{\text{Mass Number}} \times 10^4$$

As the packing fractions numbers are small, they are usually multiplied by 10^4.

When a graph is plotted. i.e. packing fractions vrs mass number of nuclides, it is seen that packing fraction is higher element of low mass numbers, (except ^{16}O, ^{12}C, ^{4}He) and it decreases rapidly with increasing mass number.

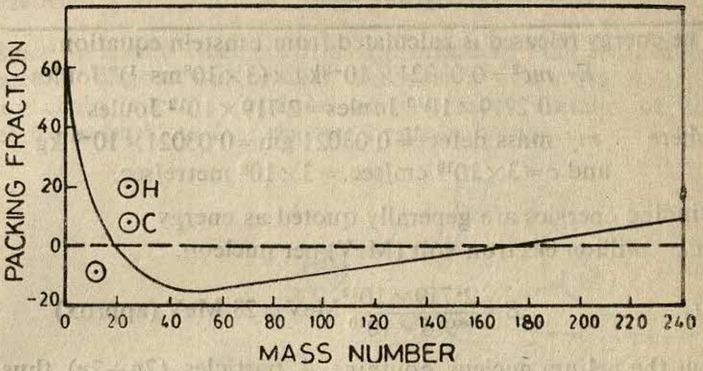


Fig. 2.3

It has been found that packing fraction is a fundamental **property** of a nucleus and is directly related to the availability of **nuclear** energy and stability. The **negative packing fraction** implies exceptional nuclear stability. On the other hand, a **positive packing fraction** (and hence mass excess) indicates that the nucleus is some what unstable.

2.24. Binding Energies

The mass of an atom, in general, is not equal to the sum of the masses of its component protons, neutrons, and electrons. If we could imagine a reaction in which free protons, neutrons and electrons combine to form an atom, we could find that for all nuclides except H the mass of the atom is slightly less than the mass of the component parts and also that a tremendous amount of energy is released when the reaction occurs. The loss in mass is exactly equivalent to the released energy, according to the Einstein, equation.

$$E = mc^2$$

energy = (change in mass) × (velocity of light)^2

The energy equivalent of the calculated loss of mass is called the binding energy of the atom or nucleus.

Examples Consider the $^{4}_{2}He$ nuclear contains $2e$, $2p$, and $2n$

Mass of 2 electrons = 2 × 0·0005486 = 0·0010972 amu
Mass of 2 protons = 2 × 1·00758 = 2·0151600 amu
Mass of 2 neutrons = 2 × 1·00893 = 2·0178600 amu

Total Mass = M = 4·03411 amu

A = The mass of He nucleus (on the ^{12}C scale) = 4·00390 amu
m = mass defect (loss in mass) = $M - A$
$m = 4{\cdot}03411 - 4{\cdot}0039 = 0{\cdot}03021$ amu

The energy released is calculated from Einstein equation.

$$E = mc^2 = 0{\cdot}03021 \times 10^{-3}\text{kg} \times (3 \times 10^8 \text{ms}^{-1})^2 \text{ Joules}$$
$$= 0{\cdot}2719 \times 10^{13} \text{ Joules} = 2{\cdot}719 \times 10^{12} \text{ Joules}$$

where m = mass defect = 0·03021 gm = $0{\cdot}03021 \times 10^{-3}$ kg
and $c = 3 \times 10^{10}$ cm/sec. $= 3 \times 10^8$ metre/sec.

Binding energies are generally quoted as energy
i.e., million electron volt (MeV) per nucleon.

or, $$E = \frac{2{\cdot}719 \times 10^{12}}{{*}9{\cdot}6 \times 10^{10}} \text{MeV} = 28 \text{ MeV (approx)}$$

But the helium nucleus contains 4 particles $(2p + 2n)$ thus the binding energy per nucleus is $\frac{28}{4}$ MeV = 7 MeV.

Binding energies of the nuclei of other atom can be calculated in a similar way. The greater the energy liberated in the formation of nuclide from nucleous, *greater is its stability.*

*electron volt (1eV) = 23·06 k cal mol^{-1} = $23{\cdot}06 \times 10^3$ cal mol^{-1}
1 Million electron volt (MeV) = $10^6 \times 23.06 \times 10^3$ cal mol^{-1}
$= 23{\cdot}06 \times 10^9 \times 4{\cdot}186$ joule mol^{-1} [1 cal = 4·186 joules.]
$= 96 \times 10^9$ J mol^{-1} $= 9{\cdot}6 \times 10^{10}$ J mole^{-1}

2.25. Nuclear Fission

The starting point in the discovery of nuclear fission can be traced to the attempts of Fermi, in 1934, to produce transuranic elements (f-block) by bombarding uranium with neutrons. However, the fission process itself was discovered in 1939 by German physicists Otto Hahn and E. Strasmann.

They found that when uranium ($^{235}_{92}U$) is bombarded with neutrons, the nucleus splits up into two almost equal fragments with the release of tremendous energy of about 200 MeV per nucleon.

Thus the process in which a heavy nucleus splits up into two nuclei *of nearly comparable masses with tremendous release of energy is called nuclear fission.*

Example : $^{235}_{92}U+^{1}_{0}n\rightarrow\left[^{236}_{92}U\right]\rightarrow^{141}_{56}Ba+^{92}_{36}Kr+3\,^{1}_{0}n+200$ Mev

Since, in fission more neutrons are produced than are needed to initiate the fission, the process becomes a chain reaction. This nuclear chain reaction produces an enormous amount of energy which forms basic nuclear reacters or atom bombs.

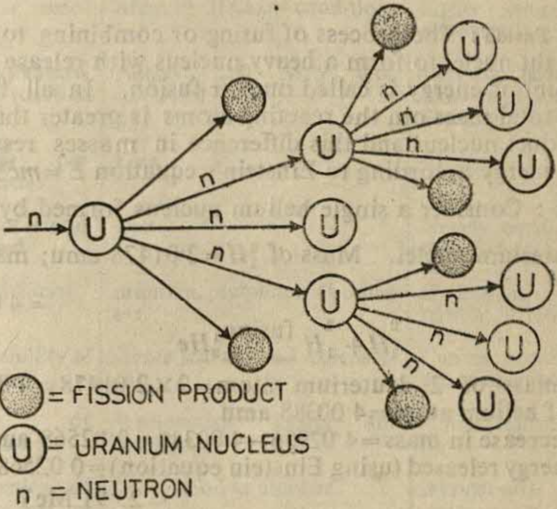


Fig. 2.4 Fission of ^{235}U.

The phenomenon of fission has two remarkable properties.

(i) The enormous energy of 200 MeV/nucleon is released, and

(ii) It is accompanied by the ejection of secondary neutrons.

Illustration : $^{235}_{92}U+^{1}_{0}n\rightarrow\left[^{236}_{92}U\right]\rightarrow^{141}_{56}Ba+^{92}_{36}Kr+3\,^{1}_{0}n+$energy

Mass of $^{235}_{92}U=235{\cdot}045733$ amu

Mass of $^{1}_{0}n=1{\cdot}008665$ amu

Total initial mass $=236{\cdot}044398$ amu

Mass of $^{141}_{56}Ba$

$=140{\cdot}9177$ amu

Mass of $^{92}_{36}Kr$

$=91{\cdot}8854$ amu

Mass of $3^{1}_{0}n$

$=3\times1{\cdot}008665$ amu

Total final mass

$=235{\cdot}829095$ amu

$$\begin{array}{ll} & 236{\cdot}044398 \\ \text{Difference} & -235{\cdot}829095 \\ \hline & =0{\cdot}2133 \end{array}$$

∴ 1 amu = 931 MeV

Energy released = 0·2133 × 931 Mev = 198·58 MeV.

Thus in the process of fission of one nucleus of uranium, about 200 MeV energy is released.

2.26. Nuclear Fusion

Nuclear Fusion : The process of fusing or combining together two or more light nuclei to form a heavy nucleus with release of tremendous amount of energy is called nuclear fusion. In all fusion processes the total mass oin the reacting atoms is greater than the mass of the product nucleus and this difference in masses results in the release of energy according to Einstein's equation $E = mc^2$.

Example : Consider a single helium nucleus formed by the fsuion of two deuterium nuclei. Mass of ${}_{1}^{2}H = 2{\cdot}01478$ amu; mass of ${}_{2}^{4}He$ $= 4{\cdot}00388$ amu.

$${}_{1}^{2}H + {}_{1}^{2}H \xrightarrow{\text{fusion}} {}_{2}^{4}He$$

Initial mass of 2 deuterium atom = 2 × 2·01478 = 4·02956 amu.
Mass of helium atom = 4·00388 amu
∴ Decrease in mass = 4·02956 − 4·00388 = 0·02568 amu.
∴ Energy released (using Einstein equation) = 0·02568 × 931 MeV
= 23·91 MeV

Thus the energy released in fusion is 23·91 MeV.
[as 1 amu = 931 MeV)]

Condition for Fusion Reaction

Usually, the lighter nuclei cannot be brought together to react because of the strong repulsive forces they experience owing to their identical nature of charges. So the fusion process can be carried out only at extremely high temperature in order to give the nuclei high *KE* to overcome these repulsive forces. These fusion reactions taking place at high temperatune of the order of 10^7 to 10^8 °C are called thermonuclear reactions. In order to initiate a thermonuclear reaction, temperature of the order of 10^7 °C and intense momentary pressures are needed and this principle Fission—Fusion process is utilized in the construction of **hydrgen bomb**.

Release of Energy : The available energy per fission of *U*-235 is about 200 MeV whereas in the energy per fusion of deuterium-deuterium atom is only 23·91 MeV. But the mass of hydrogen atom is much less than that of uranium and so the released per unit mass of material in fusion process is much greater than that in the fission process.

Comparison between Fission and Fusion

Sl. No.	*Particular*	*Fission*	*Fusion*
1.	Process	Due to the splitting of heavy nucleus into two smaller one.	Due to fusion of the light nuclei into a single heavier nucleus.
2.	Condition for nuclear reaction	Neutron spikes fissionable atom at ordinary condition.	Fusion takes place at higher temperature and pressures.
3.	Energy released per reaction	Nearly 200 MeV (for uranium).	Less and nearly 24 MeV (for deuterium-deuterium fusions).
4.	Energy per unit mass	Less	More.
5.	Rate of energy released	Less	Nearly eight times more than fission.
6.	Material used	uranium, plutonium, thorium etc.	Hydrogen, deuterium, tritium, lithium.
7.	Availabillity of material	Acute scarcity and expensive too.	Can be procured in abundance and cheap too.
8	Effect of byproduct	Radioactive wastes are harmful.	Almost harmless.
9.	Production of radioactive isotopes	Quite good in number.	Almost nil.
10	Chain reaction	Chain reaction is always possible.	Not nccessarily.
11.	Peaceful use of nuclear energy	Possible in controlled chain reaction.	Not possible.

2.27. Artificial or Induced Radioactivity

Discovery : Artificial or induced radioactivity was discovered by Curie and Joliot in 1934. They were studying the disintegration of light element by α-particles. When boron and aluminium were bombarded with α-particles, the target continued to emit radiations even after the source of α-particles had been removed. With the help of magnetic deflection experiments and ionisation measurements it was found that the radiation consisted of particles having a positive

charge and mass equal to that of electrons. These particles are known as positron.

$$ {}^{10}_{5}B+{}^{4}_{2}He \rightarrow {}^{13}_{7}N^{*}+{}^{1}_{0}n; \quad {}^{13}_{7}N^{*} \xrightarrow{t_{1/2}=10\cdot1 \text{ min}} {}^{13}_{6}C+{}^{0}_{+1}e $$

(positron)

In the case of aluminium,

$$ {}^{27}_{13}Al+{}^{4}_{2}He \rightarrow {}^{31}_{15}P^{*} \longrightarrow {}^{30}_{15}P^{*}+{}^{1}_{0}n $$

$$ {}^{30}_{14}Si+{}^{0}_{+1}e \xleftarrow{t_{1/2}=3 \text{ min}} $$

The phenomena by which even the lighter elements could be made artificially radioactive is called induced radioactivity.

The artificial radioactivity follows the same laws of decay as natural radioactivity. Unlike natural radioactive substances, which emit α, β, and γ rays, artifical radioactive substances emit elements, neutrons, positron or γ-rays.

Practically all elements can be made artificially radioactive by bombarding them with various particles. It is found that electron emission takes place in artificial radio-elements produced by (*n*, *p*), (*n*, α), (*d*, *p*) and (*n*, γ) reactions.

2.28. Production of Artificial Radioactivity

1. Artificial radioactivity by α-particle :

When light elements between *B* and *Ca* are bombarded with α particles give rise to radio elements. Many of these radio elements emit positrons but few of them electrons :

Example : (a) $ {}^{27}_{13}Al+{}^{4}_{2}He \rightarrow {}^{30}_{15}P+{}^{1}_{0}n $

$ {}^{30}_{15}P \rightarrow {}^{30}_{14}Si+{}^{0}_{+1}e $ (Positron)

(b) $ {}^{25}_{12}Mg+{}^{4}_{2}He \rightarrow {}^{28}_{13}Al+{}^{1}_{1}H $

$ {}^{28}_{13}Al \rightarrow {}^{28}_{14}Si+{}^{0}_{-1}e $ (electron)

2. Artificial Radioactivity by Proton :

Example : (a) $ {}^{11}_{5}B+{}^{1}_{1}H \rightarrow {}^{11}_{6}C+{}^{1}_{0}n $

$ {}^{11}_{6}C \rightarrow {}^{11}_{5}B+{}^{0}_{+1}e. $

(b) $ {}^{12}_{6}C+{}^{1}_{1}H \rightarrow {}^{13}_{7}N+\gamma $

$ {}^{13}_{7}N \rightarrow {}^{13}_{6}C+{}^{0}_{+1}e. $

3. Artificial Radioactivity by Deutron :

Example : (a) $^{23}_{11}Na + ^{2}_{1}H \rightarrow ^{24}_{11}Na + ^{1}_{1}H$

$$^{24}_{11}Na \dashrightarrow ^{24}_{12}Mg + ^{0}_{-1}e$$

(b) $^{26}_{12}Mg + ^{2}_{1}H \rightarrow ^{24}_{11}Na + ^{4}_{2}He$

$$^{24}_{11}Na \dashrightarrow ^{24}_{12}Mg + ^{0}_{-1}e.$$

4. Artificial Radioactivity by Neutron :

Example : (a) $^{27}_{13}Al + ^{1}_{0}n \longrightarrow ^{24}_{11}Na + ^{4}_{2}He$

$$^{24}_{11}Na \rightarrow ^{24}_{12}Mg + ^{0}_{-1}e$$

(b) $^{23}_{11}Na + ^{1}_{0}n \dashrightarrow ^{23}_{10}Ne + ^{1}_{1}H$

$$^{23}_{10}Ne \dashrightarrow ^{23}_{11}Na + ^{0}_{-1}e.$$

5. Artificial Radioactivity by γ-rays.

$$^{31}_{15}P + \gamma \rightarrow ^{30}_{15}P + ^{1}_{0}n$$

$$^{30}_{15}P \longrightarrow ^{30}_{14}Si + ^{0}_{+1}e\ .$$

2.29. Isotopes

They are different kind of atoms of the same element having the same atomic number but different mass numbers.

Example : Protium($^{1}_{1}H$) Deuterium ($^{2}_{1}H$ or $^{2}_{1}D$), and Tritium ($^{3}_{1}T$, $^{3}_{1}H$) are isotopes of hydrogen.

Characteristics of Isotopes : Isotopes have same (a) atomic number, (b) number of protons or electrons, (c) chemical properties, (d) position in periodic table but have different (a) physical properties and (b) number of neutrons.

Type of Isotopes : (1) **Non-radioctive isotopes—**

Example : (a) $^{16}_{8}O$, $^{17}_{8}O$, $^{18}_{8}O$; (b) $^{35}_{17}Cl$, $^{36}_{17}Cl$, $^{37}_{17}Cl$

(c) $^{40}_{20}Ca$, $^{41}_{20}Ca$ etc.

(ii) **Radioactive Isotopes :** This is due to loss of $(1\alpha + 2\beta)$ particles from a radioactive elements. Example

$$^{238}_{92}U,\quad ^{234}_{92}U$$

Structure of Isotopic Hydrogen

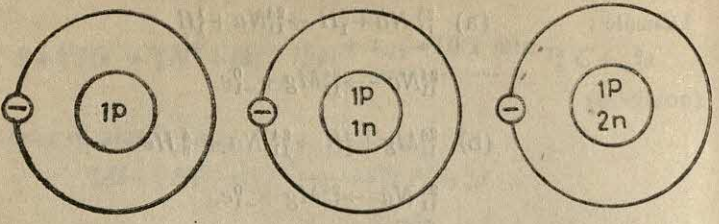


Fig. 2.5

Detection of Isotopes : Isotopes are detected by (i) Positive Rays Method and (ii) Aston Mass Spectrograph Method.

2.30. Uses of Isotopes

(a) Iodine isotopes are used in Goitre, (b) Carbon-14 is used in dating of plants (c) Cobalt isotopes are used in the treatment of cancer (d) Phosphorous-isotopes are used in Agriculture.

2.31. Carbon-Dating

The principle of this method essentially consists of determining the radioactivity of the radioactive carbon which is the constituent of all plants and animal system. Plants and animals acquire carbon—14 (a radioactive isotopes of carbon) in the following process.

Process. Carbon -14 has a half-life period of 5760 years. It is produced by cosmic ray bombardment of nitrogen gas in the upper atmosphere, represented by the following nuclear reaction.

$$ {}^{14}_{7}N + {}^{1}_{0}n \longrightarrow \underset{\substack{\text{(radioactive)}\\ \text{carbon}}}{{}^{14}_{6}C} + {}^{1}_{1}H \ (n, p \text{ reaction}) $$

$C-14$ combines with oxygen to form radioactive ${}^{14}CO_2$.

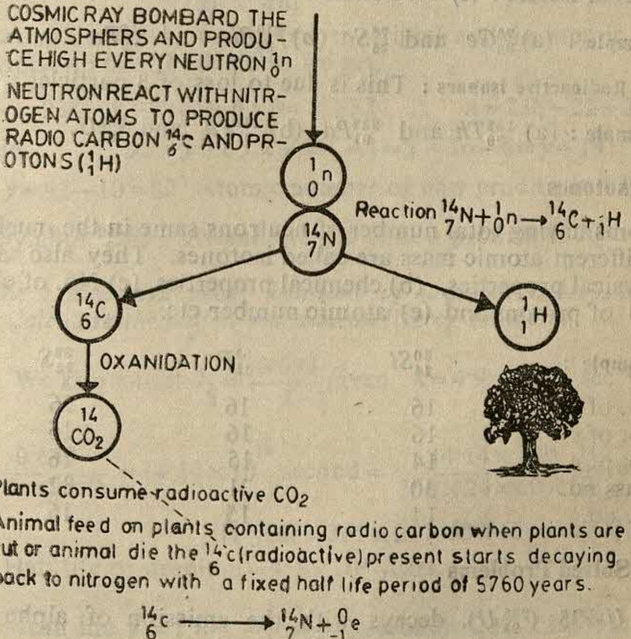
The radioactive ${}^{14}CO_2$ diffuses down the earth and is absorbed by plants. Since animals eat plants, ultimately reach the animal system. If plant or animal dies or cut (like wood or fossil), they are removed from the carbon cycle, then the intake of $C-14$ is stopped and starts decaying according to the equation.

$$^{14}_{6}C \rightarrow ^{14}_{7}N + ^{0}_{-1}e \ (t_{\frac{1}{2}} = 5760 \text{ years})$$

Thus by measuring the radioactivity and knowing the $t_{\frac{1}{2}}$ of $^{14}_{6}C$, it is possible to know when the sample was removed from the carbon cycle, using equation

$$t = t_{\frac{1}{2}} \frac{[\log_{10}(N_0/N)]}{\log_{10} 2} \quad \text{Vide equation (2.12)}$$

The method is illustrated in fig. 2.7 and is frequently employed in geological and archaeological dating of the ancient samples.


COSMIC RAY BOMBARD THE ATMOSPHERS AND PRODU-CE HIGH EVERY NEUTRON ^1_0n
NEUTRON REACT WITH NITROGEN ATOMS TO PRODUCE RADIO CARBON $^{14}_{6}C$ AND PROTONS (^1_1H)
^1_0n
$^{14}_{7}N$
Reaction $^{14}_{7}N + ^1_0n \rightarrow ^{14}_{6}C + ^1_1H$
$^{14}_{6}C$
^1_1H
OXANIDATION
$^{14}CO_2$

Plants consume radioactive CO_2

Animal feed on plants containing radio carbon when plants are cut or animal die the $^{14}_{6}C$(radioactive) present starts decaying back to nitrogen with a fixed half life period of 5760 years.

$$^{14}_{6}C \longrightarrow ^{14}_{7}N + ^{0}_{-1}e$$

Fig. 2.6. Illustration showing carbon dating method

2.32. Isobars

They are atoms of different elements having different atomic number but the same mass number.

Example : $^{40}_{18}Ar$, $^{40}_{19}K$ and $^{40}_{20}Ca$

TABLE

	Argon	Potassium	Calcium
(i) At. No.	18	19	20
(ii) No. of protons	18	19	20
(iii) No. of electrons	18	19	20
(iv) No. of neutrons	22	21	20
(v) Mass No.	40	40	40

Characteristics of Isobars : Isobars have same (a) mass number but different (b) Physical properties, (c) No. of protons, (d) No. of neutrons and (e) Chemical properties.

Types of Isobars : (i) Non-radioactive Isobars :

Example : (a) ${}^{76}_{32}Ge$ and ${}^{76}_{34}Sc$ (b) ${}^{210}_{83}Bi$ and ${}^{210}_{84}Po$

(ii) Radioactive isobars : This is due to loss of β-particles.

Example : (a) ${}^{232}_{90}Th$ and ${}^{232}_{91}Pa$ (b) ${}^{232}_{91}Pa$ and ${}^{232}_{92}U$.

2.33. Isotones.

Atoms having total number of neutrons same in the nucleus but have different atomic mass are called isotones. They also differ in (a) physical properties, (b) chemical properties, (c) No. of electrons, (d) No. of protons and (e) atomic number etc.

Example :	${}^{30}_{14}Si$	${}^{31}_{15}P$	${}^{32}_{16}S$
No. of *n*	16	16	16
No. of *p*	16	16	16
No. of *e*	14	15	16
Mass no.	30	31	32
At. no.	14	15	16

2.34. Solved Problems

1. U-235 (${}^{235}_{92}U$). decays with the emission of alpha and beta particles to form ultimately ${}^{207}_{82}Pb$. How many alpha and beta particles are emitted per atom when lead-207 is formed.

(CEE Bihar 1983; Roorkee 1985)

Sol. Let x be the number of α-particles and y be the number of β-particles emitted for converting ${}^{235}_{92}U$ to ${}^{207}_{82}Pb$

Thus, $^{235}_{92}U \rightarrow {}^{207}_{82}Pb + x\,{}^{4}_{2}He + y\,{}_{-1}^{0}e$

(α-particle) (β-particle)

Equating the mass number units (superscripts) and the atomic number (sub-scripts) of both sides, we get,

$235 = 207 + 4x + y \times 0$ or $28 = 4x$ $\therefore$ $x = 7$

Also, $92 = 82 + 2x + y \times (-1)$ or $92 = 82 + 2 \times 7 - y$

or $92 = 82 + 14 - y = 96 - y$ $\therefore$ $y = 4$

Hence $\alpha = 7$ and $\beta = 4$

2. *Uranium-*238 *(at. no.* 92) *during various disintegration steps looses* 8 α *and* 6 β *particles. What will be atomic number and atomic weight of new product ?* **(WBJEE 1983)**

Sol. $^{238}_{92}U \rightarrow {}^{x}_{y}M + 8\,{}^{4}_{2}He + 6\,{}_{-1}^{0}e$ $\left\{\begin{array}{l}\text{Here } \alpha = 8\\ \text{and } \beta = 6\end{array}\right.$

(α) (β)

Equating the mass number (super-scripts) and the atomic number (sub-scripts) units of both sides. we get,

$$238 = x + 8 \times 4 + 6 \times 0 = x + 32 \quad \therefore \quad x = 238 - 32 = 206$$

Again $\quad 92 = y + 8 \times 2 + 6 \times -1 = y + 16 - 6 = y + 10$

or $y = 92 - 10 = 82$ Atomic number of new product is 82

$\therefore$ Symbol $^{206}_{82}Pb$ Atomic weight of new product is 206

3. *The radioactive decay constant of uranium is* $4 \cdot 9 \times 10^{-18}$ *per second. Calculate the half-life and mean life of uranium.*

Sol : We know that $t_{\frac{1}{2}} = \dfrac{0 \cdot 693}{\lambda}$ given $\lambda = 4 \cdot 9 \times 10^{-18}$ sec^{-1}

$$= \frac{0 \cdot 693}{4 \cdot 9 \times 10^{-18}} = 14 \cdot 14 \times 10^{16} \text{ second} = \frac{14 \cdot 14 \times 10^{16}}{365 \times 24 \times 60 \times 60} \text{ years}$$

[1 year = 365 × 24 × 60 × 60 second]

$\therefore$ Half life of uranium $= 4 \cdot 5 \times 10^{9}$ years.

or, Mean life $T = 1/\lambda = \dfrac{1}{4 \cdot 9 \times 10^{-18}}$ second $= 20 \cdot 4 \times 10^{16}$ second

$$= \frac{20 \cdot 4 \times 10^{16}}{365 \times 24 \times 60 \times 60} \text{ years} = 6 \cdot 5 \times 10^{9} \text{ years.}$$

4. *The radioactive disintegration constant* λ *of radium-D is* $1 \cdot 13 \times 10^{-9}$ sec^{-1}. *How much time a given sample would take to reduce to* 1/10*th of its original value ?*

Sol. : We know that $N = N_0 e^{-\lambda t}$

Given $N=\frac{1}{10}N_0$; $\lambda=1{\cdot}13\times10^{-9}$ sec^{-1}

or, $\frac{1}{10}N_0=N_0e^{-\lambda t}$ or, $\frac{1}{10}=e^{-\lambda t}$

or, $10=e^{+\lambda t}$ taking log we have $\log_e 10=\log_e e^{\lambda t}=\lambda t$

or, $2{\cdot}303\log_{10}10=\lambda t$ or, $2{\cdot}303=\lambda t$

$$\text{or, } t=\frac{2{\cdot}303}{\lambda}=\frac{2{\cdot}303}{1{\cdot}13\times10^{-9}}=\frac{2{\cdot}303\times10^{9}}{1{\cdot}13}\text{ sec}$$

$$\therefore\quad t=\frac{2{\cdot}303\times10^{9}}{1{\cdot}13\times365\times24\times60\times60}\text{ years}=64{\cdot}5\text{ years.}$$

5. *A wooden article found in a cave has only* 40% as much *C*-14 *activity as a fresh piece of wood. How old is the article* ($t_{\frac{1}{2}}$ for C-14 = 5760 years)

Sol. : $N_0=100\%$, $N=40\%$ of N_0 $t_{\frac{1}{2}}=5760$ years

we know that $t_{\frac{1}{2}}=\dfrac{0{\cdot}693}{\lambda}=5760$ years

$$\therefore\quad \lambda=\frac{0{\cdot}693}{5760}=1{\cdot}203\times10^{-4}\text{ year}^{-1}$$

Substituting the values in the equation $t=\dfrac{2{\cdot}303}{\lambda}\log\dfrac{N_0}{N}$

$$t=\frac{2{\cdot}303}{\lambda}\log_{10}\frac{100}{40}=\frac{2{\cdot}303}{1{\cdot}203\times10^{-4}}(\log_{10}100-\log_{10}40)$$

$$=\frac{2{\cdot}303}{1{\cdot}203\times10^{-4}}(2-1{\cdot}60206)=7{\cdot}617\times10^{3}\text{ years.}$$

6. Carbon from the door frame of a house built at the time of Indus valley civilisation has an activity of 9·3 disintegration per minute per gram of carbon. If the house was built right after the tree was cut down, estimate how long ago the civilisation exists.

(1 gm. of carbon from living matter undergoes 15·3 disintegration per minute and $t_{\frac{1}{2}}=5760$ years.)

Sol. $t=t_{\frac{1}{2}}\dfrac{[\log_{10}(N_0/N)]}{\log_{10}2}$ Vide equation (2.12)

Given $t_{\frac{1}{2}} = 5760$ years; $N_0 = 15 \cdot 3$ disintegration per minute per gm.

$N = 9 \cdot 3$ disintegration per minute per gram

$$\text{then } t = 5760 \times \frac{\log_{10}(15 \cdot 3/9 \cdot 3)}{0 \cdot 30103} = \frac{5760 \times 0 \cdot 21621}{0 \cdot 30103} = 4137 \text{ years}$$

7. *Half-life period of a radioactive element is* 27·96 *days. Calculate the time taken by a given sample of the element to reduce to* 1/8*th initial activity.*

Sol. $$\lambda = \frac{0 \cdot 693}{t_{\frac{1}{2}}} = \frac{0 \cdot 693}{27 \cdot 96}$$

$$\text{or } \frac{N}{N_0} = e^{-\lambda t} \quad \text{or} \quad \lambda t = 2 \cdot 303 \times \log \frac{1}{N/N_0} = 2 \cdot 303 \times \log 8$$

$$\text{or } t = \frac{2 \cdot 303 \log 8}{\lambda} = \frac{2 \cdot 303 \times 0 \cdot 9032}{0 \cdot 693} \times 27 \cdot 96 = 83 \cdot 92 \text{ days.}$$

Alternatively, $\underset{\text{Original}}{1} \longrightarrow \frac{1}{2} \longrightarrow \frac{1}{4} \dashrightarrow \frac{1}{8}$

Total Time = No. of steps × half life period

$= 3 \times 27 \cdot 96 = 83 \cdot 88$ days.

8. *A radioactive sample initially contains* 4·00 mg *of* $^{234}_{92}U$ (*a*) *How much of it will remain unchanged after* 62,000 *years ?* (*b*) *What will be its* $^{234}_{92}U$ *activity at the end of that time, express your answer in curie.*

(Given $t_{\frac{1}{2}} = 2 \cdot 48 \times 10^5$ years and $\lambda = 8 \cdot 88 \times 10^{-14}$ sec^{-1})

Sol. (a) Using the fundamental relation :

$$N = N_0 e^{-\lambda t}$$

Given $t_{\frac{1}{2}} = 2 \cdot 48 \times 10^5$ years; $t = 62{,}000$ years

$$\therefore \lambda t = \frac{0 \cdot 693}{t_{\frac{1}{2}}} \times t = \frac{0 \cdot 693}{2 \cdot 48 \times 10^5} \times 62000 = 0 \cdot 173$$

Now $N = N_0\ e^{-0 \cdot 173}$. or $\frac{N_0}{N} = e^{0 \cdot 173}$

taking logarithms $\log_e \frac{N_0}{N} = \log_e e^{0 \cdot 173} = 0 \cdot 173$

or $\frac{N_0}{N} = 1{\cdot}189$ (taking antilog of $0{\cdot}173 = 1{\cdot}189$)

or $N = \frac{N_0}{1{\cdot}189} = \frac{4\text{mg}}{1{\cdot}189} = 3{\cdot}364$ mg (as $N_0 = 4$mg)

$\therefore$ Mass left unchanged $N = 3{\cdot}364$ mg $= 3{\cdot}364 \times 10^{-3}$ gm.

$\therefore$ $\therefore$ 234 gm of uranium $= 6{\cdot}023 \times 10^{23}$ atom

$3{\cdot}364 \times 10^{-3}$ gm of uranium $= \frac{6{\cdot}023 \times 10^{23}}{234} \times 3{\cdot}364 \times 10^{-3}$ atom

Activity is given by λN

$$\text{Activity} = \lambda N = 8{\cdot}88 \times 10^{-14} \times \frac{6{\cdot}023 \times 10^{23} \times 3{\cdot}364 \times 10^{-3}}{234}$$

$= 7{\cdot}69 \times 10^{5}$ disintegration per second.

1 curie $= 3{\cdot}7 \times 10^{10}$ disintegration per second (*d.p.s.*)

$$1\ d.p.s. = \frac{1}{3{\cdot}7 \times 10^{10}} \text{curie}$$

$$7{\cdot}69 \times 10^{5}\ d.p.s. = \frac{7{\cdot}69 \times 10^{5}}{3{\cdot}7 \times 10^{10}} \text{curie} = 2{\cdot}08 \times 10^{-5} \text{ curie}$$

9. *Radioactive decay is a first order process. Radioactive carbon in wood sample decays with a half life of* 5770 *years. What is the rate constant* (*in years*$^{-1}$) *for the decay ? What fraction could remain after* 11540 *years.* (IIT 1984)

Sol. For a first order reaction,

$$R = \frac{0{\cdot}693}{t_{\frac{1}{2}}} = \frac{0{\cdot}693}{5770} = 1{\cdot}201 \times 10^{-4} \text{ years}^{-1}$$

Since 11540 years contain two half-periods, its quantity after as many years will be halved twice over, the fraction that would remain will be $\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$. **one forth.**

Exercises

Long Type Questions

1. (a) Define radioactivity. **(P. U. 1980, WBJEE 1983, BIEC '85)**
   (b) List at least two main characteristics of radioactivity which distinguish it from a chemical change. **(WBJEE 1983)**
   (c) Explain the characteristic of radioactive substances. What is meant by half-life period. **(P. U. 1980)**

2. State 'group displacement law' in radioactivity. How does it predict the existence of isotopes and isobars ?. **(AISB 1982; BIEC '85)**

3. Enumerate the properties of α, β and γ-rays **(P. U. 1982, '82 Spl)**

4. Distinguish between
   (a) α-particle and Helium atom,
   (b) α-and β-particles,
   (c) Nuclear fission and nuclear fusion,
   (d) Chemical and nuclear reaction,
   (e) Artificial and natural radioactivity,
   (f) Half-life period and Average life period. **(BIEC 1985)**

5. Explain the term disintegration constant, half-life period and average life period as applied to radioactive elements. How they are related to one another.

   Prove that : $t_{\frac{1}{2}} = \frac{0 \cdot 693}{\lambda}$

   What information is available from half-life period ?

6. Write notes on : (i) Nuclide, (ii) Nucleon, (iii) Curie, (iv) Nuclear reaction, (v) Packing fraction, (vi) Mass defect, (vii) Binding energy.

7. (a) What is the meaning of 'Binding energy' ?

   (b) Which element in the periodic table have the greatest binding energy per nucleon ?

   (c) Which element has the most stable nuclei ?

8. (a) Explain what are isobars and isotons.

   (b) The constitution of nuclei of four elements is given below—

   (i) $20\,p + 15\,n$, (ii) $20\,p + 17\,n$, (iii) $20\,p + 20\,n$, (iv) $18\,p + 22n$.

Select pair of isotopes and isobars from the above, giving reasons. **(ISM. 1984).**

(c) Pick out the isotopes, isobars and isotones from the following nuclide—

${}^{3}_{1}H$, ${}^{4}_{2}He$, ${}^{14}_{6}C$, ${}^{15}_{7}N$, ${}^{238}_{92}U$, ${}^{16}_{8}O$, ${}^{130}_{56}Ba$, ${}^{210}_{82}Pb$

${}^{235}_{92}U$, ${}^{130}_{54}Xe$, ${}^{210}_{83}Bi$, ${}^{30}_{14}Si$, ${}^{40}_{19}K$, ${}^{31}_{15}P$, ${}^{40}_{18}Ar$,

${}^{32}_{16}S$, ${}^{35}_{17}Cl$, ${}^{130}_{52}Te$, ${}^{37}_{17}Cl$.

9. (a) Complete the following nuclear equations.

   (i) ${}^{27}_{13}Al + {}^{4}_{2}He \rightarrow {}^{30}_{15}P + ??$ **(AISB 1982 D B S 1980)**

   (ii) ${}^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{141}_{56}Ba + {}^{62}_{36}Kr + ?? + \gamma$ **(Roorkee 1983, AISB '82; DSB '80)**

   (iii) ${}^{23}_{11}Na + {}^{2}_{1}H \rightarrow {}^{21}_{10}Ne + ?$ **(Roorkee 1983)**

   (iv) ${}^{9}_{4}Be + {}^{4}_{2}He \rightarrow {}^{12}_{6}C + ?$ **(A. I. S. B. 1981)**

   (v) ${}^{14}_{7}N + {}^{1}_{0} \rightarrow {}^{3}_{1}H + ?$ **(I. S. C. 1983)**

(vi) $^{23}_{11}Na + ? \rightarrow ^{26}_{13}Al + ^{1}_{0}n$

(vii) $? + ^{4}_{2}He \rightarrow ^{43}_{20}Ca + ^{1}_{0}n$

(viii) $^{27}_{13}Al + ^{1}_{1}H \rightarrow ^{24}_{12}Mg + ?$ (I. S. C. 1983)

(ix) $^{232}_{90}Th \rightarrow ^{228}_{88}Ra + ??$
(x) $^{241}_{94}Pu \rightarrow ^{241}_{95}Am + ?$ (DSB 1981)

(b) Write nuclear equations for the following transformations—

(i) $^{241}_{94}Pu$ emits a Particle
(ii) $^{89}_{39}Y$ emits a positron (SSCE 1980)

(c) $^{14}_{6}C$, nuclide undergoes β-decay, what stable nuclide is formed? Demonstrate the electron balance in the equation. (Roorkee 1983)

(d) Explain with suitable examples the difference between isobars, isobars and isotones.

10. Explain why

(a) Elements shift in their position in the periodic table due to radioactivity.

(b) Lighter elements like hydrogen are suitable for carrying out fusion reactions while the heavier elemehts are suitable for fission reaction.

(c) The calculated and observed mass of atomic nuclei are different.

(d) The activity and disintegration constant of a radio element depend on its quantity.

11. State whether the following statements are True or False—

(i) γ-rays are deflected in a magnetic field.

(ii) Uranium is more radiactive than Polonium.

(iii) The *e/m* ratio of β-particle is identical with that of an electron.

(iv) α-particle have a charge of +1 and no mass.

(v) The ejection of a β-particle has no effect on the mass number of an isotope.

(vi) Shorter the half-life period, smaller is the number of atoms that are disintegrating.

(vii) Lower the binding energy of a nucleus, smaller will be the packing fraction.

(viii) The nucleus having negative packing fraction will be very stable.

(ix) If an element emits an α-particle, the daughter element belongs to the next group in the periodic table.

(x) The half-life period of the radioactive element is a characteristic property of that element.

12. (a) Match the column A with B.

A	B
1. β-particle	(a) Packing Fraction
2. X-rays	(b) Irene Curie Joliot
3. Radioactivity	(c) 0·693 T
4. Half-life period	(d) Velocity of light
5. Average life period	(e) Fission
6. Artificial radioactivity	(f) Fusion
7. Geiger Muller counter	(g) Roentgen
8. Stability of nucleus	(h) ^{206}Pb
9. Energy of sun	(i) Becquerel
10. Atom Bomb	(j) Electron
11. γ-ray	(k) λ (disintegration constant)
12. $4n+2$	(l) Detection of radioactity
13. Isotone	(m) $^{235}_{92}U$, $^{238}_{92}U$
14. Isotope	(n) $^{14}_{6}C$, $^{16}_{8}O$.

12. (b) Fill up the blanks in the following :

(a) Rates of radioactive disintegration are given in terms of............

(b) Slow moving neutrons are more............than fast moving neutrons in nuclear transformation.

(c) Though a nucleus does not contain any electron in the nucleus of a radioactive element, still it emits............

(d) β^+ particle are also called..................

(e) The number of neutron in the parent nucleus give ^{14}N on β emission is .... **(IIT 1985)**

NUMERICALS

13. Calculate the weight of ^{14}C (half life = 5,720 years) atoms which give $3{\cdot}7\times10^7$ disustagration per second. **(Roorkee 1986)**

14. At a certain instant a piece of radioactive meteral contains 10^{12} atoms. The half life period is 30 days. Calculate the number of disintegrations in the first second. **(ISM 1986)**

15. A given sample of a radioactive isotope shows an activity of 8640 counts per minutes at one time and 7620 counts per minutes one hour later. What is its half period ?

16. The half-life period of a radioactive element is 10 days. Calculate how long it takes for 90% of given mass of a this element to disintegrate ?

17. The half-life period of radiosodium ^{24}Na is 15 hours. Calculate the percentage loss in activity which occurs in a sample of Na-24 in 10 minutes.

18. The disintegration rate of radioactive element changes from an initial value of 10^4 disintegration per minute to $2{\cdot}5\times10^3$ disintegration per minute in 50 days. Calculate the disintegration constant, half-life and average life period of the element.

19. Naturally occuring carbon contains two isotopes of ^{12}C and ^{13}C, the nuclide masses of which are 12·000 and 13·0034. What are percentage of the two isotopes in a sample of carbon whose atomic mass is 12·0111.

20. One gram of $^{198}_{79}Au$ ($t_{\frac{1}{2}}=65$ hours) decays by β emission to produce stable mercurry :

(i) Write the nuclear reaction for the process.
(ii) How much mercury will be present after 260 hours. **(Roorkee 1984)**

21. The atomic weight of uranium is 238 while its atomic number is 92. Find out the atomic weight and atomic number of the daughter element if the element loses 8 α-and 6 β-particle.

22. Calculate the mass number, atomic number and group in the poriodic table for *RaC* in the following radioactive disintegration sequence—

$$^{226}_{88}Ra \xrightarrow{-\alpha} Rn \xrightarrow{-\alpha} RaA \xrightarrow{-\alpha} RaB \xrightarrow{-\beta} RaC$$ **(ISM 1984)**

Select and write the correct answer from the following :

23. The half-life period of a radioactive element is 140 days. After 560 days, one gram of the element will reduce to
(i) $\frac{1}{2}$ g (ii) $\frac{1}{4}$ g (iii) $\frac{1}{8}$ g (iv) $\frac{1}{16}$ g **(IIT 1986)**

24. (a) Radioactivity was accidentally discovered by
(i) J. J. Thom-son, (ii) Vant's Hoff,
(iii) Madam curie, (iv) Heway Beequerel

(b) Radioactive nucleus can not emit :
(i) an particles simultaneouslv
(ii) particle and rays in succession
(iii) particle and rays in succession
(iv) any two rays in succession.

25. An α-particle consists of :

(i) light rays, (ii) x-ray, (iii) positively charged particles, (iv) Negatively charged particles. **(BIEC 1983)**

26. A radioactive nucleus having excess number of neutrons decays by emitting :

(i) nucleus, (ii) photons, (iii) deutrons, (iv) electrons

27. Radioactive rays consists of :
(i) only positively charged rays.
(ii) only negatively charged rays.
(iii) positively charged, negatively charged and neutral all three types of rays.

28. Which of the following is not a radioactive substance
(i) *Be*. (ii) *Po*, (iii) *At*, (iv) P*h*.

29. Alpha particle is nothing but
(i) Helium atom, (ii) Helium nucles,
(iii) He^{+}, (iv) He^{++}. **(BHU 1983)**

30. The velocity of α-particle is
(i) the same as β particle, (ii) less than β particle,
(iii) greater than β particle, (iv) the same as γ-rays.

31. Which among the following radiation will not ionise a gas :
(i) *x*-rays, (ii) α-particle, (iii) electron, (iv) γ-rays.

32. The penetrating of γ-rays.
(i) More than α-particle, (ii) same as, β-particle
(iii) greater than, β-particle, (iv) less than β particle.

33. The radiation from a naturally occuring radioactive substance, as seen after deflection by a magnetic field in one direction are :
(i) definitely alpha rays, (ii) definitely beta rays,
(iii) both alpha and beta rays, (iv) either alpha or beta rays.
(I. I. T. 1984)

34. γ-rays have
(i) low ionizing power (ii) low penetrating power,
(iii) low velocity, (iv) high ionizing power.

35. Which of the following have the maximum penetrating power :
(i) α-particle, (ii) β-particle, (iii) neutrons, (iv) γ-rays.

36. When a readioactive element emits a β-particle from the nucleus, the new substance produced
(i) has the same atomic number. (ii) gains one neutron
(iii) gains one unit in atomic mass.
(iv) gains one unit in atomic number.

37. When a radioactive element emits an α-particle its nuclear charge is reduced by :
(i) One, (ii) three, (iii) four, (iv) two.

38. Due to α-particle emission from a radioactive atom the resulting element falls
(i) Two places left in the periodic table.
(ii) Two places right in the periodic table.
(iii) One place left in the periodic table and.
(iv) One place right in the periodic table. **(BIEC 1984)**

39. When an α particle is emitted the daughter element gets displaced in the periodic table by :
(i) one group to the left, (ii) two group to the left,
(iii) one group to the right, (iv) two group to the right.

40. When a radioaction element emit two β-particle the product will be an :
(i) Isotope, (ii) Isobar, (iii) Isotone, (iv) Isomer.

41. When a radioactive element emit one α-particle and two β-particle the product will be an
(i) Isobar, (ii) Isotope, (iii) Isotone, (iv) Isomer.

42. When $^{211}_{82}Pb$ emits a β-particle, it is converted into :
(i) $^{211}_{80}Hg$ (ii) $^{215}_{84}Po$, (iii) $^{211}_{83}Bi$, (iv) $^{211}_{85}At$.

43. The nucleide $^{232}_{90}Th$ on disintegration form stable isotope $^{208}_{82}Pb$. The number of α-and β-particles emitted are :
1. $\alpha=3;\ \beta=4$, 2. $\alpha=6;\ \beta=3$, 3. $\alpha=4,\ \beta=6$, 4. $\alpha=6;\ \beta=4$

44. A radioelement $^{241}_{94}Pu$ losses 8α-and 5β- particles, the product is
1. $^{210}_{83}Bi$, 2. $^{209}_{83}Bi$, 3. $^{206}_{82}Pb$, 4. $^{208}_{82}Pb$

45. The half life of a radioactive substance is defind as
(i) half of the time taken for the substance to decay
(ii) half of the time taken for the half of the substance to decay.
(iii) Time taken for half of the substance to decay
(iv) all of the above.

46. Half life period of a radioactive substance is equal to
(i) $0{\cdot}693\lambda$, (ii) $\lambda/0{\cdot}693$, (iii) $0{\cdot}693/\lambda$, 4. None of these.

47. Half-life period is :

(i) independent on the amount of radioactive substance taken originally.
(ii) dependent on temperature and pressure.
(iii) depend on the amount of substance taken originally.
(iv) same for all radio element. **(BIEC 1983)**

48. The half life of a radioactive substance is 18 hours. The fraction of the substance left behind after 54 hours is :

(i) 1/2, (ii) 1/16, (iii) 1/8, (iv) 1/3.

49. After one hour only 1/4th of the initial quantity of a radioactive isotope remains behind. Its half-life period is :

(i) 0·50 hour, (ii) 0·40 hour, (iii) 0·25 hour. (iv) 4 hour

50. The average life period of a radioactive element is equal to :

(i) one half of disintegration constant.
(ii) same as disintegration constant.
(iii) reciprocal of disintegration constant.
(iv) reciprocal of half life period.

51. Which of the following is correct :

(i) Half-life period$=69{\cdot}3\%\times$ Disintegration constant
(ii) Half-life period$=69{\cdot}3\%\times$ Average life period.
(iii) Half-life period$=6{\cdot}93\%\times$ Average life period.
(iv) Half-life period$=69{\cdot}3\%\times$ radioactive substance

52. In an nuclear reaction $^{14}_{7}N+^{4}_{2}He\rightarrow^{1}_{1}H+X$, the

term X is 1. $^{15}_{7}N$ 2. $^{16}_{8}O$ 3. $^{17}_{8}O$ 4. $^{19}_{9}F$

53. An isotone of $^{76}_{32}Ge$ is,

(i) $^{77}_{32}Ge$ (ii) $^{77}_{33}As$ (iii) $^{77}_{34}Se$ (iv) $^{78}_{34}Se$ **(I I T 1984)**

54. Radium, a group II A element, undergoes decay. The element formed in this decay will be in the following group.

(i) I A, (ii) III A, (iii) IV A, (iv) Zero.

55. Isobar atoms have the same :

(i) mass number, (ii) atomic weights, (iii) atomic number. **(BIEC 1983)**

56. In the case of neptunium series $(4n+1)$, the end product is :
(i) ^{206}Pb, (ii) ^{208}Pb, (iii) ^{209}Pb, (iv) ^{209}Bi

57. Which of the following is not naturally occurring radioactive series.
(i) Thorium, (ii) Actinium, (iii) Uranium, (iv) Neptunium.

58. The quantity $3{\cdot}7\times10^{10}$ disintegration per second is known as :
(i) Debye, (ii) Rutherford, (iii) Einstein, (iv) Curie

59. In the following atomic sperïes

$^{65}_{30}A$ $^{64}_{32}B$ $^{67}_{31}C$ $^{64}_{30}D$
I II II IV

Which pair are isotopes ?
(i) I and II, (ii) II and III, (iii) III and IV, (iv) I and IV.

□□□

CHAPTER 3

PERIODIC CLASSIFICATION

3.1. Introduction

After the discovery of a very large number of elements the need for their classification in smaller groups was felt. Many attempts have been made from very early times for this purpose. A few of such attempts are given below—

HISTORICAL BACKGROUND

System	*Idea*	*Examples*
1. Prout's Hypothesis (1815) (Unitary Theory)	Hydrogen atom was the fundamental unit from which all atoms were made.	Element sodium with atomic weight 23 was considred to be a product of 23 hydrogen atoms.
2. Doberneir's Triads (1829)	In the triads (certain groups of three elements with similar properties), the atomic weight of the middle element was approximately the arithmetic mean of the other two.	Ex. (i) $\underset{7}{Li}$, $\underset{23}{Na}$, $\underset{39}{K}$ (i) $\underset{32}{S}$, $\underset{79}{Se}$, $\underset{127\cdot5}{Te}$, (iii) $\underset{40}{Ca}$, $\underset{87\cdot5}{Sr}$ $\underset{137\cdot5}{Ba}$ (iv) $\underset{35\cdot5}{Cl}$, $\underset{80}{Br}$, $\underset{127}{I}$.
3. Newland's Octaves (1864)	If the known elements were arranged in increasing order of atomic weight, the eighth element standing from a given one, was a kind of repetition of the first, like the 8th note 'in the octave of music.	${}_3Li$ ${}_4Be$ ${}_5B_6C$ ${}_7N$ O_8 F_9 ${}_{11}Na$ ${}_{12}Mg$ ${}_{13}Al$ ${}_{14}Si$ ${}_{15}P$ ${}_{16}S$ ${}_{17}Cl$
4. Lothar Meyer's atomic volume curve (1869)	The properties of the elements are largely a periodic function of their atomic volumes.	He plotted the atomic volumes of the elements against the atomic weghts and found similar elements occupying similar positions on the curve. For examples the peaks are occupied by alkali metals.

System	*Idea*	*Examples*
5. Mendeleeff's classification (Periodic Law 1869)	The properties of the elements 'were periodic functions of their atomic weights.	When elements are arranged in increasing order of their atomic weight then similar kind of elements were found to reoccur after regular intervals.
6. Moseley concept (Modern Periodic Law 1913)	The properties of the elements are periodic functions of their atomic numbers.	The at. no. of an element is a more fundamental property than the ,atomic mass. Thus, the elements in the modern Periodic Table are arranged in order of their increasing at. no.

3.2. Description of Periodic Table

Group : *There are nine vertical columns. These are called groups* These are headed by the Roman numbers from I to VIII and zero.

All the groups excepting zero and VIII are divided into two subgroups *A* and *B*. Zero group consists of noble gases. Group VIII consists of transition elements. These are metals with more than one valency.

Periods : *The horizontal rows are known as periods.* There are seven periods in all. The first period is the shortest and consists of only two elements with *H* and *He*.

The second and third periods have eight elements each (from *Li* to *Ne* and from *Na* to *Ar*). These are known as short periods.

The fourth and the fifth periods consist of eighteen elements each (from *K* to *Kr* and from *Rb* to *Xe*). These are called long periods.

The sixth period is the longest and consists of 32 elements. These are from *Cs* to *Rn* and include 14 rare earth elements (also called lanthanides) from atomic number 58 to 71. 'These are placed together into one space belonging to lanthanum.

The seventh period is incomplete and consists of 17 radioactive elements. The elements beginning with atomic number 93 do not occur in nature but have been prepared artificially. These are known as transuranic elements.

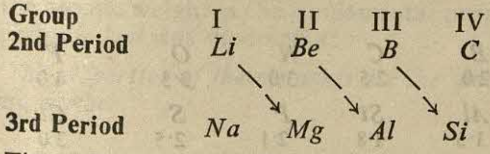
3.3. Difference between Mendeleeff's Periodic Table and Modern Periodic Table

Mendeleeff's Periodic Table	*Modern Periodic Table.*
1. It depends on atomic weight	1. It depends upon atomic number
2 It is short form of Periodic table	2. It is long form of Periodic Table
3. There are nine groups including ero	3. There are 16 groups including zero. $\frac{\text{IA to VIIA}}{7}$, $\frac{\text{IB to VIIB}}{7}$ $\frac{\text{VIII}}{3\text{ elements}}$ and zero group elements.

3.4. General Characteristics of the Periods

(i) The elements of second ($Li-F$) and third ($Na-Cl$) periods are known as Typical elements. Elements of the second period are the best representatives of their groups.

(ii) First three elements of the second period e.g. *Li*, *Be* and *B* show a diagonal relationship with elements of third period.



These elements resemble in some properties with the elements of the same group and in some properties they resemble with the element of the higher group with which they have diagonal relationship.

The elements of the third period are sometimes known as **bridge elements.**

(iii) **Gradual Change in Properties** : Elements in the same period show a gradual change in their properties with change in atomic weights.

(a) **Metallic Character** : It decreases in a period with increase of atomic number from left to right.

Na	*Mg*	*Al*	*Si*	*P*	*S*	*Cl*
Metallic	Metallic	Metallic	Non-metallic	Non-metallic	Non-metallic	Non-metallic

(b) Electropositive Nature : It decreases in a period with increase of atomic number.

Na	Mg	Al	Si	P	S	Cl
Strongly electro-positive.	+*ve*	+*ve*	Neutral	−*ve*	−*ve*	−*ve* (strongly electronegative)

(c) The Nature of Oxides : The basic nature of the oxides decrease from left to right in a period but acidic nature increases with increase of atomic number.

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
Strongly basic.	Basic	Amphoteric	Acidic	Acidic	Acidic	Strongly acidic.

(d) Valency with Respect to Hydrogen : It increases from 1 to 4 then decreases from 3 to 1 with increase of atomic number in a period :

	LiH	BeH_2	BH_3	CH_4	NH_3	H_2O	HF
Valency	1	2	3	4	3	2	1

(e) Valency with Respect to Oxygen : It increases from 1 to 7 in a period with increase of atomic number.

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
Valency	1	2	3	4	5	6	7

(f) Electronegativity : It increases in a period with increase of atomic number.

Li	Be	B	C	N	O	F
1·0	1·5	2·0	2·5	3·0	3·5	4·0
Na	Mg	Al	Si	P	S	Cl
0·9	1·2	1·5	1·8	2·1	2·5	3·0

(g) Ionisation Potential : It increases in a period with increase of atomic number.

Li	Be	B	C	N	O	F	Ne	
5·4	9·3	8·3	11·3	14·6	13·6	17·4	21·6	*eV.*

3.5. General Charcateristics of Groups

There is a gradual change in properties with rise of atomic number in the same group.

(a) Metallic Character : It increases with the rise in atomic number e.g. in Group IA sub-group from Lithium (Li) to Francium (Fr).

(b) Electropositive Nature : It increases with the rise in atomic number e.g. in IA sub-group from Li to Fr.

(c) Ionisation Potential : It decreases as the atomic number increases.

(d) Electronegativity : It decreases as the atomic number increases.

(e) **Valency** : The group number of an element indicates its valency with respect to oxygen.

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
Group	I	II	III	IV	V	VI	VII
Valency	1	2	3	4	5	6	7

3.6. Uses of the Periodic Table (Mendeleeff's P. T.)

1. Prediction of New elements. 2. Determination of atomic weights 3. Correction of atomic weights. 4. Best system for classification of elements.

3.7. Drawbacks of the Periodic Table

1. Position of Hydrogen. 2. Position of Rare Earths. 3. Position of Isotopes. 4. Anamalous pairs of elements i.e., (i) *Ar* (40), *K*(39) (ii) *Co* (59), *Ni* (58·6) (iii) *Te* (127·6) *I* (127) etc. 5. Position of VIII group elements. 6. Similar elements put apart. i.e., (i) *Cu* (IB), *Hg* (IIB) (ii) *Ag* (IB), *Tl* (IIIA) (iii) *Au* (IB), *Pt* (VIII) etc.

7. Dissimilar elements placed in the same group. i.e., *Cu*, *Ag* and *Au* are placed with alkali metals in the first group.

3.8. Modern Periodic Law

It was shown by Henry Moseley (1913) that atomic number and not the atomic weight is the fundamental property of the atom. Thus the periodic law was modified as :

"*The properties of the elements are the periodic function of their atomic number.*"

Removal of Drawbacks of Mendeleeff's Periodic Table.

Some of the defects present in the periodic classification have been removed are given below :

1. **Position of Hydrogen** : Dual behaviour of Hydrogen is explained by the fact that it has one electron in its orbit. When it loses one electron it gives H^+ and behaves like alkali metals and when it gains one electron it gives H^{-1} and behaves like halogens. The dual behaviour of hydrogen is due to this peculiar electronic arrangement.

2. **Position of Isotopes** : There were no place for isotopes of the same element Since the isotopes of the same element possess the same atomic number, they must occupy one place in the periodic table.

3. **Anomalous Pairs** : Certain elements of higher atomic weight were placed before those having less value.

Ar (39·9)	Zero group	*Co* (58·9)	VIII group	*Te* (127·6)	VII group
K (39·1)	*I* group	*Ni* (58·7)		*I* (127·0)	VII group

But it has been found that elements having higher atomic weights possess lower atomic number and consequently must occupy their desired positions in the periodic table.

4. Position of VIII Group Elements : In long periods, 18 elements are to be distributed among 8 groups, Groups I – VII get two elements each and zero group contains only inactive element, the rest of the three elements are placed at one place in a new group, known as VIII group. This lack of space justifies the inclusion of this group in the periodic table.

5. Position of Rare Earths : Since rare earth elements have same chemical properties, hence they are placed in IIIB of Periodic Table.

6. Position of Transuranic Elements : The number of valency electrons in the case of all these elements remains the same although atomic number increases. Since they possess the same number of valency electrons their chemical behaviour is also similar. This justifies their position in the periodic table.

Long Form of PERIODIC TABLE (Bohr's Table)

It is mechanically an extended form of Mendeleeff's table which was developed by the help of **Rang** (1893), **Warner** (1905), **Bury Bohr** (1921) and many others. This is shown in the table on the following pages.

3.9. Characteristics of long form of Periodic table or Modern Periodic table.

(i) In this table the elements are arranged in increasing order of their atomic number.

(ii) The elements are placed in 16 vertical columns called groups i.e., IA, IIA, IIIB, IVB, VB, VIB, VIIB, VIII, IB, IIB, IIIA, IVA, VA, VIA, VIIA, 0.

All groups excepting VIII and zero are sub-divided in *A* and *B*.

(iii) Sub-group *A* (IA, IIA ...... VIIA) elements are known as *normal elements*. They have complete inner core. Their outermost orbit is incomplete.

(iv) Sub-group *B* (IIIB to VIIB), VIII group, IB and IIB elements are known as *transition elements.* They have generally vacant *d*-orbitals.

(v) Zero group elements are called inert gases (Noble gases).

(vi) The lanthanides and Actinides have been placed separately in two different rows just below the table.

(vii) Each period starts with alkali metals and ends to Noble gases.

(viii) In VIII groups three elements are placed together due to their close similarity in their properties.

(ix) There are seven periods in this table.

(a) First period contains 2 elements (b) second and third period contain 8 elements each. (c) Fourth and fifth period contains 18 elements each. (d) Sixth period contains 32 elements. (e) Seventh period is an incomplete period.

3.10. Types of Elements :

In the long form of the periodic table, the elements have been divided into following four blocks.

1. **s-block Elements** : These elements belong to I A and II A groups of periodic table. They are twelve in number. Their outer sub-shell contains 1 or 2 electrons.

TABLE

IA ns^1	IIA ns^2
Lithium (*Li*)	Berylium (*Be*)
Sodium (*Na*)	Magnesium (*Mg*)
Potassium (*K*)	Calcium (*Ca*)
Rubidium (*Rb*)	Strontium (*Sr*)
Cesium (*Cs*)	Barium (*Ba*)
Francium (*Fr*)	Radium (*Ra*)

2. **p-block-Elements** : These are elements of III A to VII A group of periodic table. Their outer p-sub-shell contains 1 to 5 electrons.

TABLE

III A p^1	IV A p^2	V A p^3	VI A p^4	VII A p^5
B	*C*	*N*	*O*	*F*
Al	*Si*	*P*	*S*	*Cl*
Ga	*Ge*	*As*	*Se*	*Br*
In	*Sn*	*Sb*	*Te*	*I*
Tl	*Pb*	*Bi*	*Po*	*At.*

3. ***d*-block Elements** : In the long form of periodic table, these elements are placed collectively between III B to II B. They are characterised by the atoms in which two outer most shells are incomplete. They are the atoms of those elements in which an inner ‘*d*’ orbitals is present but it is incomplete. These are *outer transition* elements.

TABLE

III B	IV B	VB	VI B	VII B	VIII			IB	IIB
d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
Sc	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Co*	*Ni*	*Cu*	*Zn*
Y	*Zr*	*Nb*	*Mo*	*Tc*	*Ru*	*Rh*	*Pd*	*Ag*	*Cd*
La	*Hf*	*Ta*	*W*	*Re*	*Os*	*Ir*	*Pt*	*Au*	*Hg*
Ac									

4. **f-block Elements** : Their three outermost electron shells are incomplete. The elements of *f* block are characterised by the filling up of ‘f’ sub shell. This block consists of 14 *lanthanides* (Atomic number 58-71) nnd 14 *actinides* (Atomic number 90-103). All these are known as *inner transition* elements.

TABLE

Lanthanides (4*f*)	*Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu* 58 59 60 61 62 63 64 65 65 67 68 69 70 71
Actinides (5*f*)	*Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw* 90 91 92 93 94 95 96 97 98 99 100 101 102 103

Summary of Long Form of Periodic Table

TABLE

S. No.	*Group*	*Electronic configuration*	*Name of the Block*
1	I *A* and II *A*	ns^1, ns^2, $n=1$ to7	*s*-block elements.
2	III *A*, IV *A*, V *A* VI *A*, VII *A* and Zero.	$ns^2\ np^{1-6}\ n=1$ to6	*p*-block elements.
3	I*B* – VII *B*, VIII	$ns^{1-2}(n-1)d^{1-10}$ $n=4, 5\ 6$	*d*-block elements.
4	Lanthanides and actinides	$ns^{1\ to\ 2}\ (n-2)f^{1-14}$	*f*-block elements

Note—There are two conventions for numbering group.

(a) According to first convention, groups are numbered as IA, IIA, IIIB, IVB, VB, VIB, VIIB, IB, IIB, IIIA, IVA, VIA, VIIA and 0 (zero).

(b) According to second convention, group are numbered as IA, IIA, IIIA, IVA, VA, VIA, VIIA, VIII, IB, IIB, IIIB, IVB, VB, VIB, VIIB and 0 (zero).

Hence in some books, it is mentioned that nitrogen, phosphorus etc. belong to VA but in other books they belong to VB. Similarly *F.*, *Cl*, *Br*, I belong to VIIA and VIIB both.

But now a days block of elements indicates their group.

(c) Most of the elements in the periodic table are transition elements.

3.11 Defects of Long Form of Periodic Table

The defects still persist in the table are :

(i) No definite position of hydrogen can be assigned.

(ii) It does not include lanthanides and actinides in the main table.

(iii) It does not reflect the electronic configuration of the various elements.

3.12. Characteristics of *s* and *p* Block Elements

(a) *s*-block Elements :

1. All of these elements are metals (excepting *H*).

2. Elements of IA are known as alkali metals and IIA are known as alkaline earth metals.

3. Elements of IA belong to *s*-block and their positive valency is +1. Elements of IIA belong to *s*-block and their positive valency is +2.

4. **Atomic radii**—The values of atomic radii increases in the group IA $H(0{\cdot}37) \rightarrow Cs\,(2{\cdot}25)$ IIA $Be(0{\cdot}9) \rightarrow Ba(1{\cdot}93)$ Å due to the increase in the shell numbers.

5. **Electropositive character**—Increases gradually in group IA ($Li \rightarrow Cs$) IIA ($Be \rightarrow Ba$) top to bottom.

6. Recently it has been reported that *s*-block elements form complex compounds.

7. They are colourless.

8. They generally form electrovalent compounds.

9. Their oxides are basic.

10. Their electronegativity decreases in a group I *A* $Li\,(1{\cdot}0) \rightarrow Cs\,(0{\cdot}7)$ top to bottom.

11. Ionization Potential. decreases in the groupes $Li(5{\cdot}4) \rightarrow Cs(3{\cdot}9)$.

12. In a group (IA, IIA) the reducing character increases because their electropositive character increases.

13. Electron affinity : decreases in a group.

14. Metallic character increases in a group.

(b) *p*-Block Elements :

The electronic configuration of outermost shell is from ns^2np^1 to ns^2np^6. Elements having ns^2np^6 configuration are inert gases (Noble gases) (except Helium $1s^2$) and they have been placed in zero group. Elements of ns^2np^1 to ns^2np^5 are called **normal elements** This includes metals and non-metals both. The main characteristics of these elements are—

1. The *non-metallic* character increases from elements of IIIA to VIIA.

2. The *electronegative* nature increases from elements of IIIA to VII *A*.

3. Generally their oxides are acidic but some like ZnO, Al_2O_3, SnO_2, PbO_2 are amphoteric.

4. They form *covalent compounds* amongst themselves and electrovalent compounds with *s*-block elements.

5. They are generally non-metals or metalliods but some heavy elements like lead, bismuth are metals.

6 They posses *definite valency* but some elements such as Nitrogen and phosphorus exhibit variable valency.

7 *Ionization Potential* increases from elements of IIIA the VIIA.

8. *Electron affinity* increases from elements of IIIA to VIIA.

3.13. Periodicity of Properties

(A) Atomic size/Radii

Atomic radii (or covalent radii) is the distance between the centre of the nucleus of an atom and its outermost electron shell. It indicates the size of the atom.

Ionic Radii : Ionic radii of an element is the size of the ion formed as a result of the removal of all the valency electrons.

Periodic Variations of Atomic and Ionic Radii

Atomic or ionic radius is a periodic function of their atomic number, i.e. it changes with the change of atomic number in the periodic table as shown below :

(a) **In a period** : *Atomic and ionic radii both decreases from left to right across a period in the periodic table when we consider only normal elements* e.g., in the elements of 2nd period the covalent radii decreases as we move from *Li* to *F* as shown below,

Element of 2nd period :	*Li*	*Be*	*B*	*C*	*N*	*O*	*F*
Covalent radii (Å) :	1·23	0·90	0·82	0·77	0·75	0·73	0·72

————————Values decreasing————→

Thus in any period the alkali metals (that are present at the extreme left of the periodic table) have the *largest size* while the halogens (that are present at the extreme right, excluding the *zero group* elements) have the *smallest size*.

Explanation : We know that as we proceed from left to right in a period, the electrons are added to the orbitals of the same main energy level, with the addition of each electron, their nuclear charge (i.e. atomic number) is increased by one. The increased nuclear charge attracts the electrons more strongly close to the nucleus and thus decreases the size of the atoms.

In a group : *On moving down a group of regular elements, both atomic and ionic radii increase with increasing atomic number* e.g. in the elements of IIA Group both covalent and ionic radii of M^{2+} ions increase when we pass from *Be* to *Ba*.

Elements of IIA group :	*Be*	*Mg*	*Ca*	*Sr*	*Ba*
Covalent Radii (Å) :	0·90	1·36	1·74	1·91	1·98
Ionic radii of M^{2+} cations (Å) :	0·31	0·65	0·96	1·13	1·35

————Values increasing————→

Explanation : When we proceed from top to bottom in a group, the following two opposite forces act simultaneously.

(i) On proceeding downwards in a group, the electrons are added to higher main energy levels which are, on the average, farther from the nucleus. This effect decreases the electrostatic attraction between the nucleus and the valence-shell electrons and this decreased electrostatic attraction increases the atomic and ionic radii.

(ii) The nuclear charge (i.e. atomic number) increases as we proceed from top to bottom. This increase in nuclear charge decreases the atomic and ionic radii.

(i) The cations have smaller size than corresponding neutral atoms.

(ii) The anions have bigger size than corresponding neutral atoms.

(iii) The lower the charges, greater will be the size of the ion.

Explanation : O^{-2}, F^{-1}, N^{-3}, Na^{+}, Mg^{+2} have same number of electrons but N^{-3} is the largest (due to smallest charge) and Mg^{+2} is the smallest (due to largest charge).

(B) Ionization Potential or Ionization Energy

Definition : *The amount of energy required to remove the most loosely bound electron (i.e. the outermost electron) from an isolated gaseous atom of an element in its lowest energy state (i.e. ground state) to produce a cation is known as ionisation potential or ionisation energy of that element.*

It is generally represented as *I*, or *IP* and is measured in electron volt (*eV*). When it is expressed in K. cals. per gm. atom, it is known as **ionisation energy**.

$M \rightarrow M^{+} + e^{-1}$ (1st *I. P.* I_1) $M^{+} \rightarrow M^{++} + e^{-1}$ (2nd *I.P.* I_2)

$M^{++} \rightarrow M^{+++} + e^{-1}$ (3rd *I.P.*I_3) $\therefore\ I_1 < I_2 < I_3 < \ldots\ldots$

This process is an endothermic process, since the energy is supplied to effect it.

It can be measured experimentally by placing atoms in a gas discharge tube and gradually increasing the potential between the two plates. From this voltage the I.P. is calculated.

Factors Affecting Ionization Potential or Ionization Energy

(i) Charge on the nucleus, (ii) Type of electrons involved,
(iii) completely filled or half-filled orbitals,
(iv) screening effect, (v) Atomic radius,
(vi) Principal quantum number.

Factors Affecting the Ionization Potential and its Periodic Variations

(i) Charge on the Nucleus : (i.e. nuclear charge) and Variation in a Period. The greater the charge on the nucleus of an atom, the more difficult it would be to remove an electron from the atom and hence greater would be the value of ionisation potential.

Thus the value of ionisation potential generally increase in moving from left to right in a period. Since nuclear charge of the elements (i.e , atomic number) also increases in the same direction, (which increases electrostatics attraction between the outermost electrons and nucleus) eg.

Elements of 2nd period :	*Li*	*Be*	*B*	*C*	*N*	*O*	*F*	*Ne*
Nuclear charge :	+3	+4	+5	+6	+7	+8	+9	+10
Ionization potential (eV) :	3·4	9·3	8·3	11·3	14·5	13·6	17·4	21

(ii) Type of Electrons Involved : *s*-electrons being closer to the nucleus, are held more tightly than *p*, *d* or *f*-electrons. Hence ionisation potential decreases in the order $s > p > d > f$.

Example : The ionisation potential corresponding to the removal of 2*p* electron of Boron ($B \rightarrow 2s^2p^1$) is 8·3 eV while those corresponding to the removal of two 2*s*-electrons are 25·1 and 37·9 eV.

(iii) Completely filled and half-filled Orbitals : According to Hund's rule atoms having half-filled or completely filled orbitals are comparatively more stable and hence more energy is needed to remove an electron from such atoms. The ionisation potential of such atoms is therefore, relatively higher than expected normally from their position in the periodic table.

Example : A few irregularities that are seen in the increasing values of ionisation potential along a period can be explained on the basis of the concept of half filled and completely filled orbitals, e.g. *Be* and *N* in the second period and *Mg* and *P* in the third period have slightly higher values of ionisation potentials than those normally expected. This is explained on the basis of extra stability of the completely filled 2*s*-orbital in *Be* ($Be \rightarrow 1s^2 2p^1$) and 3*s*-orbitals in Mg ($Mg \rightarrow 3s^2$) and of half-filled $2p$ orbitals in N ($N \rightarrow 2s^2\ 2p^3$) and $3p$-orbital in P ($P \rightarrow 3s^2\ 3p^3$).

(iv) The Screening Effect of the Inner Electrons on the Valence Electrons and Variation in a group : The greater the number of the electrons in the inner shells, the smaller will be the ionisation potential.

As we move down a group, the number of inner shells increasing and have the ionisation potential tends to decrease, e.g. :

Elements of IIA group :	*Be*	*Mg*	*Ca*	*Sr*	*Ba*
Number of inner shell :	1	2	3	4	5
Ionization potential (eV) :	9·3	7·6	6·1	5·7	5·2

————————Decreasing——————→

(v) Atomic Radius and Variation in a group : With the increse in atomic radii, the ionisation potential decreases. This is because of the fact that in case of larger atoms the attraction between the nucleus and outermost electron is less and hence it is easier to remove an electron from a larger atom than from a smaller one. *Thus on moving from top to bottom in a group, the ionisation potential of the element decrease with the increase of their atomic radii e.g.* :

Elements of IA group :	*Li*	*Na*	*K*	*Rb*	*Cs*
Covalent radii (A) :	1·55	1·90	2·35	2·48	2·67
Ionization potential (*eV*) :	5·3	5·1	4·3	4·2	3·9

————————Decreasing——————→

(vi) Principal Quantum Number (*n*) and Variation in a group : Higher the value of n, the lower will be the amount of energy required to remove the electrons i.e., its ionisation potential will be lower.

Thus on moving from top to bottom in a group as the value of n for the valence electrons increases, ionisation potential decreases, as is evident from the following examples :

Examples : (a) Values of first and second ionisation potentials of Li ($Li \rightarrow 1s^2 2s^1$) are 5·3 eV and 75·6 eV respectively 5·3 eV is the energy required to remove $2s$ electron when $n=2$ and 75·6 eV when $n=1$.

(b) First I P. of Ne ($Ne \rightarrow 2s^2 2p^6$) and Ar ($Ar \rightarrow 3s^2 3p^6$) are 21·6 eV and 15·8 eV respectively. Obviously n for Ne ($=2$) is smaller than Ar ($=3$), I P. of Ne ($=21·6$ eV) is higher than that of Ar ($=15·8$ eV).

Application of the Concept of Ionisation Potential

(i) *To explain the trend from metallic to non-mettalic character of elements from left to right in a period.*

At the left of a period in a periodic table, we have the elements with low ionisation potential values. These elements, therefore, react by loosing electrons and thus form ionic bonds. These elements are, therefore typical metals.

Near the end of a period, since the elements have high values of ionisation potential, these tend to take up electrons and thus form negative ions. Thus these elements are typical non-metals.

(ii) **To determine the Number of Valence Electrons in an Atom** : For example in case of Li, Ist I. P. $= 5{\cdot}4$ eV and 2nd I. P. $= 75{\cdot}6$ eV. These values show that one electron can much more readily be removed than the other. Thus there is only one electron in the valence shell of Li atom.

(iii) **Relative Reactivity of Element** : Elements having high values of ionisation potential are less reactive (e.g. inert gases), while those having low values are very reactive (e.g. Alkali metals and Alkaline earth metals).

(iv) **Reducing Power of an Elements** : Lower the value of ionisation potential of an element, the greater is its reducing power, since easily removed electron from the elements would be accepted by the oxidising agent thereby, lowering its oxidation state.

$$\underset{\text{(reducing agent)}}{A^\circ} \xrightarrow[\text{(oxidation of } (A^\circ))]{-e} A^+ \quad \cdots \text{(i)}$$

$$\underset{\text{(oxidising agent)}}{B^\circ} \xrightarrow[\text{(reduction of } B^\circ)]{+e \text{ from equ}^n\text{(i)}} B^{-1} \quad \cdots \text{(ii)}$$

(v) **Basic Character of Elements** : Lower the value of I. P. of an element, the greater will be the basic character of the element concerned.

(C) Electron Affinity or Affinity Energy

Definition : *The amount of energy released when an electron is added to an isolated neutral gaseous atom in its lowest energy state* (i.e. ground state) *to produce an anion is called its electron affinity* or *affinity energy.*

It is generally represented as E_A or E and is measured in electron volt (eV) or Kilo cal. per gm atom. This electron affinity can be defined by the equation.

$$\underset{\substack{\text{(Neutral gaseous}\\\text{atom)}}}{A\,(g)} + e^-\,(g) \rightarrow \underset{\text{(Anion)}}{A^-(g)} + \text{Energy released } (EA \text{ or } E)$$

The above process by which the neutral gaseous atom adds an electron is an exothermic process, since energy is released in it. Since electron affinity represents the energy released, it is represented with a negative sign placed before it. Electron affinity just defined as actually *first electron affinity* (E_1), since it corresponds to the addition of one electron only. In the process of adding an electron to an anion, A^- (g) against the electrostatic repulsion between the electron being added and the negative charge on A^- (g) ion, energy instead of being added and the negative charge on A^- (g) ion, energy instead of being released is supplied to A^- (g) to form A^{2-} (g).

$$A\text{ (g)}+e^{-1}\text{ (g)}\longrightarrow A^-\text{ (g)}+\text{Energy released}$$
$$A^-\text{ (g)}+e^-\text{ (g)}+\text{Energy supplied}\rightarrow A^{2-}\text{ (g)}$$

Energy supplied in the process to convert A^- (g) to A^{2-} (g) is called *second electron affinity*, E_2 of A. Since E_2 is the energy absorbed, it is given a positive sign.

Factors Influencing the Magnitude of Electron Affinity

The magnitude of E is influenced by a number of factors such as :

(i) Atomic size,
(ii) Effective nuclear charge,
(iii) Screening effect by inner electrons.

Periodic Variations

(a) In a group : *In moving down a group electron affinity values generally decreases, e.g.* $E_{Cl}>E_{Br}>E_I$. *This is due to the steady* increase in the atomic radius of the elements.

Exceptions : There are, however, some exception to this general rule as is evident from the following examples :

(i) Although the elements of second period of the periodic table are relatively smaller in size than those of the third period, yet E values of elements of second period are smaller than the E values of third period of element. This is due to the smaller size of second period of element give a very much higher value of charge densities for the respective negative ion.

A high value of electron density is opposed by the inter electrons in repulsive forces.

(ii) From tables it clearly shows that $E_{Cl}>E_F$. The lower value of E for F is probably due to the electron-electron repulsion in relatively compact $2p$ orbital of F-atom.

$$\therefore\ E_{Cl}>E_F>E_{Br}E_I.$$

(b) In a period : *Electron affinity values generally increase on moving from left to right in a period in the periodic table.*

Exceptions : There are, however, exception also to this general rules e.g. :

(i) Be and Mg have their E values equal to zero. Since Be and Mg have completely filled s-orbitals ($Be\rightarrow 1s^2\ 2s^2$, $Mg\rightarrow 1s^22s^22p^63s^2$) the additional electron will be entering the $2p$-orbital in case of Be

and 3*p*-orbital in case of *Mg* which are of considerably higher energy than 2*s*-orbitals respectively.

(ii) Similarly in case of inert gases in which the *ns* and *np* orbitals are completely filled (ns^2np^6 configuration) the incoming electron must go into an electron shell having a larger value for the principal quantum number, *n*. Thus inert gases also have their *E* values equal to zero.

(iii) Nitrogen and phosphorous have unexpected lower values of electron affinities. This is because of the presence of *half filled* 2*p*-orbitals which are relatively more stable and hence to which it is difficult to add an additional electron.

Effect of Electron Affinity Concept of Chemical Behaviour

(i) The higher the values of *E* of an element, greater would be its capacity to accept an electron, i.e., the element will behave as a strong oxidising agents.

(ii) In general, with the increase of the electron affinity difference, the amount of ionic character decreases or covalent character increases.

(D) Electronegativity

When two atoms which are not identical, e.g. *H* and *Cl*, form a covalent bond, the electrons forming the bond are not equally shared. The atom with the larger share in the electron pair becomes negatively charged with respect to the second atom. In other words *Cl* atom has greater electronegativity than *H* atom.

Definition : *Thus the electronegatively of an atom is a measure of its power to attract electrons to itself in a covalent bond.*

The numerical value of this property depends upon the ionisation potential and the electron affinity. To measure electronegativity of an atom **Linus Pauling** developed an arbitrary scale, known as *electronegativity scale*. On this scale inert gases have no electronegative value. Fluorine possesses the highest value of 4·0 while caesium has lowest value i.e., 0·7.

Generally in a group it decreases from top to bottom due to increase in the size of the atom. In a period electronegativity increases with increase of atomic number.

Applications of Electronegativity Concept

(i) Higher the electronegativity of an element, greater is the acidic nature of their oxide.

(ii) In a compound if electronegativity difference between the two atoms is large, the compound is ionic in nature.

Relation Between I. P. *Ea* and *En*.

According to Mulliken, $En = \frac{\text{I. P.} + Ea}{2}$

According to Pauling, $En = \frac{\text{I. P.} + Ea}{5{\cdot}6} = \frac{\text{I P.} - (-Ea)}{5{\cdot}6}$

where I. P. and *Ea* are expressed in units of electron volt.

1. *An element A has ionisation potential* 13·0 *eV and electron affinity* −5 *eV. Calculate the electronegativity of A.*

Sol. $En = \frac{\text{I. P} + Ea}{5{\cdot}6} = \frac{\text{I. P.} - (-Ea)}{5{\cdot}6} = \frac{13{\cdot}0 - (-3{\cdot}8)}{5{\cdot}6} = \frac{16{\cdot}8}{5{\cdot}6} = 3.$

(E) Volatility

Elements having less melting and boiling points are more volatile and vice versa

Thus, volatility of metals generally increases down in a group except IB and IIB.

Volatility of non-metals generally decreases from top to bottom in a group.

Volatility increases with the decrease in electronegativity of the central atoms e.g.

2. *Volatility* : $CO_2 > SO_2 > NO_2$

(F) Solubility

Greater the difference in electronegativity between bonded atoms, greater will be the ionic character of the bond and greater the solubility in water. e.g. $C_2H_5OH > CO_2 > CH_4$

Note : There are others factors on which solubility depends they are solubility product, Lattice energy, hydration energy, polarizibility, *H*-bonding etc.

(G) Solvation Energy/Hydration Energy

Ions in aqueous solutions are always surrounded by a sheath of water molecules. Some water molecules are bound to the ions by co-ordinate bonds and some by Van der Waal's forces and energy is released when the hydration process takes place. The hydration is written for example : $Na^+ \text{ (g)} + \text{water} \rightarrow Na^+_{aq}$.

'aq' signifies water, without specifying any particular number of molecules, since this is difficult to estimate exactly. During hydration, the heat of hydration is evolved which varies from ion to ion and the following *generalisation may be made* :

(i) For ions of the same charge, the heat of hydration is inversely proportional to the ionic radius.

(ii) For ions of the similar radius, the heat of hydration is proportional to the charge on the ion.

TABLE

Hydration Energy, Ionic Radius and Ionic Charge

Ion	H^+	Li^+	Na^+	K^+
Hydration energy (k cal mole^{-1})	260	120	93	73
Ionic radius (Å)	—	0·6	0·95	1·33
Ion	Mg^{2+}	Ca^{2+}	Sr^{+2}	Ba^{2+}
Hydration energy (k cal mole^{-1})	474	395	354	326
Ionic radius (Å)	0·65	0·99	1·13	1·35

In periodic table as the size of the atoms or ions increases the hydration energy decreases. Thus the order of the hydration energy is,

$$Cs^+ < Rb^+ < K^+ < Na^+ < Li^+$$
$$I^- < Br^- < Cl^- < F^-$$

(H) Melting and Boiling Points

(i) Generally melting point and boiling point decrease in a group from top to bottom for non-transition metals.

Example : $Li > Na > K > Rb > Cs > Fr$

(ii) For transition metals the melting and boiling points usually increase from top to bottom. But there are *several exceptions.*

(iii) Among the inert gas elements the melting point and boiling point inereose as the atonic number increases.

e.g. $He < Ne < Ar < Kr < Xe < Rn$;

(iv) In periods, there is no definite trend of m. pt. and b. pt. but in many cases m. pt. and b pt. first increase and then decrease.

(v) The boiling points of elementary gases decrease as the molecular weights increase.

e.g. $Cl_2 > O_2 > N_2$

(I) Lattice Energy

Larger the size of metallic atom, lower the value of its lattice energy. In a periodic group containing metals, lattice energy decreases from top to bottom due to the corresponding increase in atomic size.

(a) **Lattice Energy of Metals :** Metals having larger values of lattice energy have higher m. pt. and b. pt. Thus in a periodic group containing metals, the m. pt and b. pt. decrease from top to bottom.

(b) **Lattice Energy of Non-metals :** The lattice energy increases from top to bottom in a periodic group containing non-metals and hence the melting and boiling points increase in the same order. For example, the trend in lattice energy in the halogen family is :

$$F < Cl < Br < I$$

The trend of lattice energy among some alkali metal halides are :

$$NaI < NaBr < NaCl < NaF$$

(J) Metallic Character

(i) Metallic character decreases from left to right across a period because atomic size decreases and ionisation energy increases.

Ex :

$$Li > Be > B > C > N$$
$$Na > Mg > Al > Si > P$$

The non-metallic character changes in the reverse orders.

Note : (i) The reactivity of metal in solid state generally increases from top to bottom in a group in periodic table because of decrease in their ionisation energy. It may be noted that smaller the I.P./IE. of a metal, larger is the reactivity in solid state. However, there are some *notable exceptions* to this rule.

Exceptions : 1. *Au* is less reactive than *Ag*
2. *Hg* is less reactive than *Cd*
3. *Pb* is less reactive than *Sn*.

This is due to higher I.E. of *Au*, *Hg* and *Pb* as compared to those of *Ag*, *Cd* and *Sn* respectively.

(ii) The *reactivity of non-metals* generally depends on its electronegativity. The larger is the electronegativity, larger is the reactivity. As the electronegativity of the elements in a sub-group decreases downwards, their reactivity also decreases in the same direction.

Example : (a) F_2 is more reactive than Cl_2 in group VIIA.
(b) O_2 is more reactive than 'S' in group VIA.

Exception : Phosphorus is more reactive than nitrogen in group VA. Hence there is *no rule* for the reactivity of metals and non-metals in a periodic table. These are only guide line.

(ii) Metallic character increases from top to bottom in a group because the atomic size increases and ionisation energy decreases e.g. metallic character increases as

$$Li < Na < K < Rb < Cs$$
$$C < Si < Ge < Sn < Pb$$

Non-metal (metal)

The metallic character changes in the reverse order.

(iii) *The most electropositive elements are found in the lower left of the periodic table and the most non-metallic in the top right.*

(iv) Transition elements are metals.

XI. DENSITY : Density of elements in a group generally increases because of larger increase in atomic mass than in their atomic volumes. Thus, the densities of alkali metals of group IA are given below :

Elements	*Li*	*Na*	*K*	*Rb*	*Cs* (IA)
Density	0·534	0·97	0·86	1·52	1·87

Elements	*Be*	*Mg*	*Ca*	*Sr*	*Ba* (IIA)
Density	1·86	1·74	1·54	2·6	3·74

Thus '*K*' is exception in group IA and *Mg*, *Ca* are in group IIA.

(K) Nature of Oxides

Generally acidic nature of oxides of elements increases in a period from left to right but basic nature increases in a sub-group from top towards bottom because of the increasing electropositive character of elements.

(L) Atomic Volume

It is the volume in ml occupied in the solid state by one mole atom of the element. It first decreases and then increases as we go from left to right across any row of the periodic table. In a group its value is found to increase with an increase in atomic number.

3.13. Types of Elements on the Basis of Electronic Configuration

There are four types of elements based on their complete and incomplete electronic shells :

(1) First Type : (Inert gases/Noble gases)—Their outermost shell is complete with ns^2p^6 and thus have stable configuration. They are

inert gases and except helium all have 8 electrons in their outermost shell. Helium has 2 electrons. They thus have the configuration ns^2p^6 in outer most shell.

Because of the stability of their electronic configuration they do not enter into ordinary chemical reactions. They constitute the zero group on the periodic table.

(2) **Second Type : (Representative or Normal element) :** All of their shells except the outermost are complete. The electronic configuration in the outer quantum levels of the atoms of these elements include from ns^1 (except $1s^2$ for *He*) to ns^2np^6.

They thus enter into chemical combination to acquire 8 electrons in the outermost orbit or to acquire *sp* configuration by losing, gaining or sharing of electrons. For example hydrogen, alkali metals, IA and alkaline earths IIA are *s*-block (the normal elements) while from IIIA to VIIA are *p*-block elements because they have from 1 to 5 electrons in their outer most sub-shell.

(for details see Art 3. 18)

(3) **Third Type : (Transition elements) :** The electronic configuration of their outer shells are given by a general structure $(n-1)\,d^{1-9}$ ns^{1-2}. They are termed *d*-block elements. They are also known as outer transition elements.

3.14. Characteristics of Transition Elements

As in all transition elements the penultimate shell of electrons is expanding, they resemble in their physical and chemical properties as given below :

(i) **Metallic Character :** These are all metals which are maleable, ductile and good conductors of heat and electricity. They form alloys.

(ii) **Physical Constants :** These are heavy metals with high melting and boiling points; zinc (*Zn*), cadmium (*Cd*) and mercury (*Hg*) have lower melting points because their subshell is complete.

(iii) **Reactivity :** They exhibit a tendency to remain unreactive or noble.

(iv) **Colour :** Their compounds are usually coloured.

(v) **Variable Oxidation state :** They exhibit variable oxidation state.

(vi) **Magnetic properties :** Most of these elements are paramagnetic because of the presence of unpaired electrons in their orbitals. Iron and cobalt are ferromagnetic and can be magnetised.

(vii) They generally form complex compounds.

(viii) They have tendency for forming alloys.

(ix) They act as catalyst.

(x) Their I.P./I.E. is intermediate between *s*- and *p*-blocks.

(4) **Fourth Type : (Lanthanides and Actinides or inner Transition Elements)** : In these elements, the three outermost orbits are incomplete i.e., *f*-block elements because their antipenultimate (third from the outermost) shell is being expanded (18 to 32) by addition of *f*-electrons and include rare earths (At. No. 58 to 71) and actinides (At. No. 89 to 103). Their two outermost orbits are exactly identical to one another. The regular filling of 4 *f*-orbitals in lanthanides and of 5*f*-orbital in actinides accounts for their striking resemblance in most of their properties.

3.15. Bridge Elements

The few elements of the third period of the periodic table are sometimes known as **bridge elements** because they resemble with elements of A and B sub-group both. For example Magnesium is known as bridge element because it resembles with Calcium (IIA) and Zinc (IIB)

$$\begin{tikzcd}[column sep=small, row sep=tiny] & Ca\ Sr\ Ba\ \text{(IIA)} \\ Mg \arrow[ur, dash] \arrow[dr, dash] & \\ & Zn\ Cd\ Hg\ \text{(IIB)} \end{tikzcd}$$

Resemblance of Magnesium with Calcium.

(i) Both are *s*-block elements. (ii) Both have two electrons in the outermost orbit. (iii) Both forms colourless compounds.

Resemblance of Magnesium with Zinc.

1. Magnesium salts give pink colour in cobalt chloride test and zinc gives green colour in cobalt chloride test.

2. $MgSO_4\ 7H_2O$ is isomorphous with $ZnSO_4.7H_2O$.

3.16. Typical Elements

Mendeleeff regarded the elements with low atomic weight in each group, particularly the first elements, as typical elements. But it is found that the first element in each group does not truely represent the behaviour of other elements in the same group and in fact resembles in many respects with the second element in next higher group. Thus the elements in the third series of the periodic table from sodium to chlorine are known as typical elements.

The remarkable features of these elements are :

They exhibit the properties of the group such as valency, electrochemical character etc.

3.17. Diagonal Relationship

It is a relationship of few elements of second and third period of the periodic table.

Group	IA	IIA	IIIA	IVA
2nd Period	*Li*	*Be*	*B*	*C*
	↘	↘	↘	
3rd Period	*Na*	*Mg*	*Al*	*Si*

Reaeon : On moving in a period, increase in ionic charge takes place with decrease in ionic sizes. This increases its polarising power. While in a group the increase in ionic size takes place giving decrease in polarising power. Thus on moving diagonally these two opposite charges partly checks each other making no marked change in properties.

3.18 Types of Elements in the Periodic Table

(At a glance or in a nutshell.)

1. **Alkali Metals** : *Li*, *Na*, *K*, *Rb*, *Cs*, *Fr* (a naturally radioactive elements) (most electropositive) They give alkalis with H_2O.

$$Na + H_2O \rightarrow NaOH + H_2$$

2. **Alkaline earth metals** : *Be*, *Mg*, *Ca*, *Sr*, *Ba*, *Ra* (a radioactive elements) (Form an alkaline solution with H_2O, found on earth surface).
3. **Coinage metals** : *Cu*, *Ag*, *Au* (Gr IB)
4. **Transition metals** : Show variable oxidation states. They give coloured ions and form complex compounds.

	Cr,	*Mn*,	*Fe*,	*Co*,	*Ni*,	*Au*	*Cu*
Oxidation state (O.S)	(3, 6)	(2, 3, 4, 7)	(2, 3)	(2, 3)	(2, 4)	(1, 3)	(1, 2)

5. **Metalliods** : (like metals and non-metals)
   As (arsenic), *Ge*, *Sb*
6. **Halogens** : F_2, Cl_2, Br_2, I_2 and *At* (a naturally radioactive element).
7. **Most electropositive** (+ve) **Element in** P. T. *Cs* (*Fr* Francium is a radioactive element).
8. **Most electronegative element** : Fluorine.
9. **Most conductive metal** : *Ag*.
10. **Most conductive non-metal** : Graphite (Element, allotropes of *C*).
11. **Liquid non-metal** : Bromine.
12. **Liquid metal** : *Hg* (Mercury) at ordinary temperature.
13. **Element kept in water** : Phosphorus P_4 (white or yellow).
14. **Element kept in kerosene oil** : *Na*, *K*, *Rb*, *Cs* (Gr. IA).
15. **Element sublimes** : Iodine (at ordinary temperature).
16. **Rare earths or lanthanides** : **Atomic number** 58 to 71.

17. **Actinides :** After *Ac* (89)→ Atomic number (90 to 103).
18. **Bridge metal :** *Mg* (number elements of Third period of *PT*).
19. **Noble metals :** *Au*, *Pt*, etc.
20. **Noble gases :** or **inert gases,**

He, *Ne*, *Ar*, *Kr*, *Xe*, *Rn* (Radon).

21. **Man made elements :** After atomic number 92. Uranium onward.
22. **Radioactive elements :** (natural) *Po*, *At*, *Rn* (gas), *Fr*, *Ra*, *Ac*, *Th*, *Pa*, *U*.
23. **Elements showing diagonal relationship :**

Li-Mg	*Be-Al*	*B-Si*
I	II	III

24. **Amphoteric metals :** *Zn*, *Al*, *Sn*, *Pb*, (non-metal – *Si*).
25. **Aanamalous pairs—**

(a) *Ar*, *K* (b) *Co*, *Ni* (c) *Te*, *I*.

26\.

At. No.	**Few New elements.**
101	Mendelevium (*Md*)
102	Nobelium (*No*)
103	Lawrencium (*Lr*, *Lw*)
104	Kurchatovium (*Ku*)
105	Hahnium (*Ha*)
106	Not named as yet.

3.19. Some Typical Problems with Answers

1. *Why is the second* IP/IE *higher than that of first* IP/IE ?

Ans. This is due to two reasons : (a) It is more difficult to remove an electron from a positively charged particle than from a neutral atom, (b) the size of the ion, M^+ is lesser than that of the atom *M* and hence it becomes more difficult to remove an additional electron due to stronger nuclear attraction.

2. *Why is the* IP/IE *of N greater than that of oxygen* ?

Ans. The elements with either completed sub-shells or half completed sub-shells are more stable than others. Nitrogen has got 2*p* half completed sub-shell whereas oxygen has not got such arrangement.

N Atomic number 7 $1s^2\ 2s^2\ 2p_x^1\ p_y^1\ p_s^1$ (stable)
O Atomic number 8 $1s^2\ 2s^2\ 2p_x^2\ p_y^1\ p_z^1$ (unstable)

In case of nitrogen, more energy is required to remove electrons hence its IP/IE is higher than oxygen.

3. *Why Be (Beryllium) has got higher* IP/IE *than Boron ?*

Ans. Beryllium has its 2 '*s*' sub-shell completed where as Boron has got incomplete $2p$-sub-shell. Hence Beryllium is more stable than Boron. Hence Beryllium has higher I.P./I.E. than Boron.

Be – Atomic number 4 $1s^2\ 2s^2$,
B – Atomic number 5 $1s^2\ 2s^2\ 2p_x^1\ p_y^0\ p_z^0$.

4. *The first and second ionisation energies of Mg are* 178 *and* 348 k cal/Mole *respectively. Calculate the energy in* eV *required for the following reaction.*

$$Mg \rightarrow Mg^{2+} + 2e$$

Ans.

$$Mg \rightarrow Mg^{+} + e \ldots .178 \text{ k cal} \qquad .. \quad (1)$$
$$Mg^{+} \rightarrow Mg^{+2} + e \ \ldots .348 \text{ k cal} \qquad .. \quad (2)$$

Adding (1) and (2) we have

$$Mg \rightarrow Mg^{2+} + 2e \ldots .526 \text{ k cal}$$

Now, 1 calorie = 4·18 joule and 1 eV = 96 48 kJ.
Hence, the energy required in eV.

$$E = 526 \times 10^3 \text{ cal.} = 526 \times 10^3 \times 4{\cdot}18 \text{ Joul.}$$
$$(1 \text{ eV} = 96{\cdot}48 \times 10^3 \text{ J})$$

$$E = \frac{526 \times 10^3 \times 4{\cdot}18}{96{\cdot}48 \times 10^3} = 22{\cdot}8 \text{ eV}.$$

5. *Arrange the following according to the* **instructions** *given* :

(i) PbO, MgO, ZnO (in the order of increasing basic nature)
(ii) Na, Al, Mg (in the order of increasing density)
(iii) Zn, Al, Cu (in the order of activity with dil. HCl)
(iv) N_2, O_2, Cl_2 (in the order of increasing boiling point)
(v) NH_3, H_2O, CH_4 (in the order of increasing m. p)
(vi) Graphite, Cu, S (in the order of increasing electrical conductivity)
(vii) $AgCl$, $PbCl_2$, $NaCl$ (in the order of increasing solubility in water)
(viii) Al, Na, Fe (in the order of increasing reactivity with moist air)
(ix) NH_3, N_2, H_2O (in the order of increasing boiling point)
(x) Pb, Al Cu (in the order of decreasing density)
(xi) CO_2, CH_4, C_2H_5OH (in the order of decreasing solubility in water)
(xii) NO_2, K_2O, ZnO (in the order of increasing basicity)
(xiii) $CaSO_4$, $BaSO_4$, Na_2SO_4 (in the order of decreasing solubility in water)
(xiv) Al, Pb, Fe (in the order of increasing density)
(xv) Zn, Na, K (in the order of decreasing electropositive character)
(xvi) Br, I, F, Cl (in the order of increasing atomic size)
(xvii) Cu, Fe, Mg (in the decreasing electropositive character)
(xviii) Na_2O, MgO, Al_2O_3 (in the order of increasing basicity)
(xix) Na, Li, K (increasing order of atomic size)
(xx) Hg, Na, Cu (increasing order of density)

(xxi) Na, Cu, Zn (increasing electropositive character)

(xxii) Br_2, Cl_2, H_2 (increasing boiling point)

Sol. (i) $PbO < ZnO < MgO$ (Mg – IIA, Zn – IIB, Pb – IVA; their electropositive character and basic nature of their oxides increase)

(ii) $Na < Mg < Al$ (density amongst metals increases along the period due to decrease of atomic size with increase of atomic number)

(iii) $Cu < Zn < Al$ (electropositive reactivity towards acid increases with decrease in I.P)

(iv) $N_2 < O_2 < Cl_2$ (mol. wt. increases)

(v) $CH_4 < NH_3 < H_2O$ (mol. wt. increases as also H-bonding)

(vi) $S <$ Graphite $< Cu$ (metallic character increases)

(vii) $AgCl < PbCl_2 < NaCl$ (increasing polarizibility)

(viii) $Al < Fe < Na$ (electropositive character increases)

(ix) $N_2 < NH_3 < H_2O$ (in H_2O there is an association of molecules due to H-bonding and that is less in NH_3 and no H-bonding in the case of N_2)

(x) $Pb > Cu > Al$ (Pb is a heavy metal, Al is a light metal)

(xi) $C_2H_5OH > CO_2 > CH_4$ (alcohol is miscible with water in all proportion due to H-bonding, while CO_2 forms H_2CO_3 with H_2O whereas CH_4 is insoluble in water)

(xii) $NO_2 < ZnO < K_2O$ (K is strongly metallic than Zn, whereas N is a non-metallic).

(xiii) $Na_2SO_4 > CaSO_4 > BaSO_4$ (as the anions are identical so solubility decreases as size of cation increases)

(xiv) $Al < Fe < Pb$ (Pb is a very heavy metal, Al is a light metal)

(xv) $K > Na > Zn$ (electropositive character decreases, as I. P. increases)

(xvi) $F < Cl < Br < I$ (atomic size increases from top to bottom in a group)

(xvii) $Mg > Fe > Cu$ (electropositive character decreases as I. P. increases)

(xviii) $Al_2O_3 < MgO < Na_2O$ (basic character increases as electropositive character increases)

(xix) $Li < Na < K$ (atomic size increases as we move from top to bottom)

(xx) $Na < Cu < Hg$ (Na is a light metal whereas Hg is one of the heavy metal)

(xxi) $Cu < Zn < Na$ (as I. P. decreases, electropositive character increases)

(xxii) $H_2 < Cl_2 < Br_2$ (usually boiling point increases as molecular weight increases)

6. *Account for the following* : (*Limit your answer within Two to Three lines*)

(i) The first electron affinity of nitrogen is negative.

(ii) The electron affinity of chlorine is greater than fluorine.

(iii) I. P. of Boron is less than Beryllium.

(iv) The atomic radius generally increases in a group from top to bottom and decreases in a period from left to right.

(v) Zero group (inert gases) is in extreme right in P. T. but their size increases instead of decreasing trend.

(vi) Non-metallic oxides are generally acidic.

(vii) Metallic oxides are generally basic.

(viii) I. P., Ea and EN of the elements increases in a period from left to right and decreases in a group from top to bottom.

(ix) The transition metals' compounds are coloured.

(x) Br_2 is a liquid but I_2 is a solid in VIIA group of P. T.

Ans. (i) The E. C. of nitrogen $(1s^2 2s^2 2p_x' p_y' p_z')$ is stable. When electron is added to it, it becomes unstable so it will resist in accepting an electron. Hence energy is needed in adding an electron in it. Therefore 1st Ea is negative.

(ii) See electron-affinity.

(iii) $B_5 - 1s^2 2s^2 2p^1$; $Be_4 - 1s^2 2s^2$. Since the removal of electrons from s-orbital (stable) needs more energy than electrons from p-orbital.

(iv) In a group orbit number changes and the electron remains the same in outermost orbit so size increase from top to bottom.

In a period, the atomic number increases, hence effective nuclear charge increases. Therefore the nuclear attraction increases and size decreases.

(v) In the case of zero group elements the inter electronic repulsion exceeds the attractive force between electrons and protons. Hence the size increases instead of decreasing trend.

(vi) Non-metals generally form covalently bonded oxides. Covalent oxides are acidic oxides.

(vii) Metals generally form ionic oxides. Ionic oxides are generally basic.

(viii) They are inversely proportional to the radius of the elements. The radius of the element decreases in a period from left to right. Hence they increase.

(ix) The colour of transition metals compound can be explained on the basis of (a) charge transfer, (b) on the basis of d-d-transition.

(x) As we go from top to bottom Vander waal's attraction increases and intermolecular space decreases, due to this Br_2 is liquid and I_2 is solid.

QUESTIONS.

Long Type :

1. (a) What is Modern Periodic law ? **(P. U. 1982 S; M. U. '81)**

(b) How atomic radii changes with increase in atomic number in a period and a group ? **(P. U. 1982 S)**

(c) Write down the general electronic configuration of normal elements, inert elements, transitional elements and inner transitional element. **(P. U. 1982 S)**

(d) Discuss the position of hydrogen in periodic table. **(P. U. 1›82 S)**

(e) What are characteristics of Modern periodic table ? **(M. U. 1981)**

2 (a) Explain : The properties of elements are the periodic functions of their electronic configuration. **(P. U. 1980 A)**

(b) Classify the elements on the basis of their electronic configuration. **(Mithila U. 1978; B. U. '80; P. U. '80 A)**

(c) How does I. P. change for the elements in a group of the periodic table ? Why is the I. P. of the elements of zero group so high ? **(P. U. 1980 A)**

3. (a) What are the trends of variation of the atomic size of elements in the periodic table along a series and along a group ? **(I. M. S. 1982)**

(b) Give reason for the variation of atomic size along a series. **(I M.S. 1982)**

(c) What is the relation between atomic size and metallic character of an element ? **(I. M. S. 1982)**

4. Arrange *Al*, *Cu*, and *Fe* in increasing order of their

(a) melting point, (b) prices, (c) specific gravities, (d) electrical conductivities, (e) production in India. **(B. I. T. Mesra 1983)**

5. (a) What do you mean by ionization potential ? What are the two factors which influence ionization potential ? **(R U. 1980; BIEC 1985)**

(b) Why do halogens have higher electron affinity ? How does this property change as we move from chlorine to iodine and why ? **(R U. 1980)**

(c) Why are some elements called transition elements, ? How have they been placed in periodic table ? **(R. U. 1980)**

(d) Put together the elements belonging to the same sub group given below :

Atomic number 3, 12, 17, 25, 37, 53, 56 and 75 **(R. U. 1980)**

6. (a) What are *s*, *p*, *d* and *f* block element ? **(I. S. M. 1984)**

Give the main characteristic of *s*, *p* and *d* block elements. **(I. S. M. 1984)**

(b) Discuss the position of hydrogen and inert gases in the periodic table. **(I. S. M. 184)**

Hint : See hydrogen and inert gas chapter.

(c) Explain what changes in atomic radii and electron affinity take place when one moves from left to right in a period of the table. Give reasons for these changes. **(I. S M. 1984)**

7. (a) Arrange the following in the increasing order of property indicated.

(i) HCl, HF, HI and HBr—acid strength

(ii) I_2, F_2, Br_2 and Cl_2—reactivity.
Give reason for your answer. **(Roorkee 1984)**

(b) Arrange the following in increasing order of the property indicated :

(i) Li, Be and B—ionization energy
(ii) Cs^{+}, K^{+} and Cl^{-}—size. **(Rookee 1984)**

8. What do you mean by electron affinity and electronegativity ? How are they related with each other ? **(BIEC 1984)**

9. Give an account of the history of classifying elements. Describe in detail the contribution of Mendeleeff in the field. What are the advantages and anomalies of the classification given by Mendeleeff ?

10. What is the modern periodic law ? How does it differ from Mendeleeff's periodic law ? How has it helped in the eliminatation of defects of Mendeleeff's periodic table ?

11. Discuss the periodicity of the elements with reference to (a) I.P., (b) E.A., (c) E. N. and (d) Atomic size in the periodic table.

12. (i) State and explain Mendeleeff's Periodic law. How has this been modified later on ?

(ii) How has the periodic table been useful for the study of chemistry ?

13. (a) What are the main features of the periodic table ? Discuss its importance.

(b) What is modern periodic law ?
(c) Name the different types of elements based on electronic configuration.
(d) What are the discrepancies in the Mendeleeff's periodic table :

14 Explain the following :

(1) Nitrogen has got higher I. P. than oxygen.
(2) Chlorine has higher electron affinity than fluorine.
(3) First I. P. of element is lower than second I. P.
(4) Atomic size decreases in a period but increases in group.

15. Arrange the following according to instruction given in the bracket.

(i) CO_2, NO_2, SO_2 (increasing acidic nature).
(ii) Cl_2, F_2, Br_2 (increasing acidic nature).
(iii) CaO, MgO, BaO (decreasing basic nature).
(iv) KOH, $Mg(OH)_2$, $NaOH$ (increasing solubility in water).
(v) NH_3, CO_2, HCl (increasing rate of diffusion).
(vi) F_2, Cl_2, Br_2 (Decreasing electron affinity).
(vii) C, N, O (increasing I. P.).
(viii) N, F, O, (increasing electronegativity).
(ix) O, S, Se (increasing reactivity).
(x) Cu, Ag, Au, (increasing density).
(xi) Ag, graphite, diamond (decreasing conductivity nature).
(xii) Ba, Sr, Ca (increasing m. p.).
(xiii) Cl, I, Br (Decreasing density).
(xiv) Mg, Na, Al (increasing atomic size).

16. Write notes on :

(i) Typical elements, (ii) I. P., (iii) Ea, (iv) Atomic size.

17. Discuss the periodicity in properties of elements on the basis of

(a) Ionisation potential, (b) Electronegativity,
(c) Electron affinity, (d) Atomic size.

18. How will you explain that atomic number is more important than atomic weight in studying the properties of the elements ? How anomalies of Mendeleeff's P. T. were removed ?

Short Type Questions. :

19. How many groups and periods are there in Mendeleeff's periodic table ? How many elements are there in 4th and 6th group of the table ?

20. How many total periods are there in Mendeleeff's periodic table and how many elements are placed in each period ?

21. Mention two defects of Mendeleeff's P. T. and how these are removed by modern periodic table.

22. Carbon is a non-metal while lead is a metal. Explain this fact.

(**Hint** : The metallic character or electropositive nature increases with increasing atomic number in sub-group.)

23. Explain what changes in atomic radii take place when one moves from left to right in a period of the periodic table. Give reasons for these changes.

24. Write notes on (a) Diagonal relationship, (b) Bridge elements, (c) Typical elements, (d) Transition elements.

25. Mention two characteristics of *s* and *p*-block elements.

26. What do you know about normal elements ? Do they exhibit variable valency ? Name two elements which show variable valency.

27. "The properties of elements are the periodic function of their atomic numbers." Comment giving examples.

28. Name (a) Liquid metal, (b) liquid non-metal, (c) two amphoteric metals, (d) one metalloid, (e) four elements showing allotropy, (f) one element which is kept in water, (g) one element which has highest I. P. in P. T., (h) one element which has highest electron affinity.

29. **Fill in the blanks :**

(i) Third period contains.........elements.

(ii) Law of octaves was given by..........

(iii) Iron is a.........block element.

(iv) The modern periodic law is based on.........

(v) The I. P..........in group but it.........in period.

30. From the following list of elements select the members of the *p* and *d*-blocks.

$Z=1$, $Z=20$, $Z=35$, $Z=30$. ($Z=$at. no.)

31 What is the basis of classifying elements into *s*, *p*, *d* and *f*-blocks ?

32. Match the column *A* with *B*

Column A	*Column B*
(i) *F*	(a) elements of *d*-block.
(ii) *Cl*	(b) most conductive metal.
(iii) *Cr*	(c) highest electronegative.
(iv) *Ag*	(d) fundamental property of atom.
(v) Atomic number	(e) highest electron affinity.

33. Match the colum *A* with *B*.

A	*B*
(1) Law of triad	(a) Newland
(2) Law of octaves	(b) Moseley
(3) Law of atomic volume	(c) Mender leeff
(4) Periodic law	(d) Lothemeyer
(5) Modern periodic law	(e) Doberenier.

34. Match the colum *A* with *B*.

A	*B*
(1) Highest I. P.	(a) MgO
(2) Highest Ea.	(b) As
(3) Highest En	(c) He
(4) Metalloid	(d) NO
(5) Amphoteric metal	(e) CO
(6) Acidic oxide	(f) Cl
(7) Basic oxide	(g) F
(8) Neutral oxide	(h) Zn

Select and Write the Correct Answer

35. Transitional metals have incomplete orbitals in :

(1) 4*s* (2) 3*s* (3) 3*p* (4) 3*d*. **(BIEC 1983)**

36. On moving in a periodic table from left to right, metallic character

(1) increases (2) decreases. **(BIEC 1983)**

37. Metalloid is :

(1) Fe (2) Co (3) Ni (4) 86. **(BIEC 1933)**

38. Diagonal relationship in its periodic table is shown by

(1) $Na-Mg$ (2) $Ca-Zn$ (3) $Al-C$ (4) $Li-Mg$. **(BIEC 1983)**

39. Moseley's law is based on

(1) atomic volume
(2) ionization potential
(3) relation of X-ray frequency with the position of elements in periodic table. **(BIEC 1983)**

40. Which is the fundamental property of an element out of the following ?

(1) Atomic weight (2) Atomic number (3) Molecular weight.
(4) Density. **(BIEC 1984)**

41. Elements are arranged in the periodic table according to :

(1) increasing molecular weight (2) decreasing atomic weight
(3) increasing valency (4) increasing atomic number.

42. The elements on the right side of periodic table are :

(1) Non-menals (2) Metals
(3) Transition elements (4) Metalloid elements.

43. The elements with atomic number 3, 11, 19, 37, 55 are all

(1) inert gases, (3) light metals, (3) metalloids, (4) transition elements
(5) alkali metals.

44. Which one of the following will have largest size ?

(1) *Br*, (2) *I*, (3) *I*, (4) *F*.

45. Electronegativity is the measure of the capacity of an atom to :

(1) repel electrons, (2) attract electrons, (3) share electrons with another
(4) combine with proton atom.

46. The heaviest atom amongst the four below is

(1) *Ra*, (2) *U*, (3) *Hg*, (4) *Pb*.

47. As one moves along a given row in the periodic table, ionisation energy :

(1) increases from left to right, (2) remains unchanged, (3) increases than decreases, (4) decreases from left to right.

48. Which of the following has got highest electron affinity ?

(1) *Cl*, (2) *F*, (3) *S*, (4) *Br*, (5) *I*, **(MDAT 1982)**

49. Which of the following statement about alkali metals is wrong ?

(1) they are *s*-block element. (2) they have one electron more than preceding inert gases. (3) they are kept in kerosene oil. (4) they have one electron less than inert gases.

50. Which element has the highest electronegativity ?

(1) *F* (2) *He* (3) *Ne* (4) *Na*. **(NCERT 1981)**

51. Which of the following has got highest I. P. ?

(1) *N* (2) *O* (3) *C* (4) *B*.

52. In the periodic table of elements going downwards :

(1) electronegativity will increase (2) ionic radius will increase
(3) reactivity will increase (4) ionisation potential will increase in fluorine group. **(NCERT 1981)**

53. The ionisation energy of an atom is the energy :

(1) needed to add an electron to the atom.
(2) needed to transfer an electron from one orbit to another.
(3) needed to convert the atom into a radioisotope.
(4) Just enough to cause an electron to escape from the atom.

54. In correct order of second ionization potential of carbon, nitrogen, oxygen and fluorine is

(1) $C > N > O > F$ (2) $O > F > N > C$
(3) $O > N > F > C$ (4) $F > O > N > C$. **(IIT 1981)**

55. The law of triad is applicable to.

(1) chlorine, bromine and iodine, (2) hydrogen, oxygen and nitrogen,
(3) sodium, neon, calcium, (4) none of the above. **(MET Andhra 1980)**

56. Thallium shows different oxidation states because.

(1) of inert pair effect (2) it is a transitron metal
(3) it is amphoteric in nature (4) it is highly reactive (AIIMS 1980)

57. The ionization energy of nitrogen is larger than that of oxygen because of :

(1) greater attraction of electrons by the nucleus.
(2) the size of the nitrogen atom being samller.
(3) the half filled *p*-orbitals possess extra stability.
(4) greater penetration effect. (AIIMS 1980)

58. The hydration energy of *Mg* is larger than that of

(1) Al^{3+} (2) Na^{+} (3) Be^{2+} , (4) Mg^{2+}. (IIT 1984)

□□□

CHAPTER 4

THE CHEMICAL BONDING

4.1. Introduction

The simple definition of valency, namely, the combining capacity of an element with respect to the number of hydrogen atoms with which an atom of an element combines, does not explain as to why elements have different valencies and how chemical compounds are formed. This definition of valency does not enable us to find out the true valency of elements which form a number of compounds with hydrogen.

Thus carbon forms compounds like CH_4 (methane), C_2H_6 (ethane), C_2H_4 (ethylene), C_2H_2 (acetylene) etc. where their valency should be 4, 3, 2 and 1. Actually in all these compounds, the valency of carbon is 4.

With the knowledge of the structure of atom, the tendency of elements to combine was clearly understood and the electronic theory of valency was put forward by *Kossel* and *Lewis* in 1916. The valency is, therefore, defined as the number of electrons taking part in bond formation.

Note : (1) There is difference between oxidation state (O.S.) and valency as shown earlier.

(2) The valency of an element can never be negative, zero and fraction. It is always a whole number.

3. The O.S. and valency of some underlined elements are given.

Elements underlined	*O.S.*	*Valency*	*Elements underlined*	*O.S.*	*Valency*
$\underline{S}_8$	0	2	$\underline{C}_3H_8$	—8/3	4
$H_2\underline{O}_2$	—1	2	$\underline{C}_6H_{12}0_6$	0	4
			$\underline{C}\,H_3\underline{C}\,OOH$	0	4
$\underline{C}_2H_4$	—2	4	$Ca\underline{C}_2$	—1	4

4.2. Basis of electronic theory of valency

(i) The valency of an element depends upon the number of electrons in the outermost orbit which are called *valency electrons.*

(ii) The electrons in the outermost orbit of inert gases (i.e. 2 for *He* and 8 for the rest of elements) form most *stable structure.*

$He_2 = 2$ or $1s^2$
$Ne_{10} = 2, 8$ or $1s^2, 2s^22p^6$
$Ar_{18} = 2, 8, 8$ or $1s^2, 2s^22p^6, 3s^23p^6$
$Kr_{36} = 2, 8, 18, 8$ or $1s^2, 2s^22p^6, 3s^23p^63d^{10}, 4s^24p^6$
$Xe_{54} = 2, 8, 18, 18, 8$ or $1s^2, 2s^22p^6, 3s^23p^63d^{10}, 4s^24p^64d^{10}, 5s^25p^6$
$Rn_{86} = 2, 8, 18, 32, 18, 8$ or $1s^2, 2s^22p^6, 3s^23p^63d^{10}, 4s^24p^64d^{10}4f^{14}, 5s^25p^65d^{10}, 6s^26p^6$

This inactivity or reluctance to undergo chemical combination by the inert gases is entirely due to their saturated outermost orbits.

(iii) The atoms of other elements, having incomplete electronic shells tend to acquire the structure of nearest inert gases. It is this tendency of atoms which causes them to combine chemically.

Elements having unstable Electronic Configuration→	(a) By transference of electrons (electrovalency)	Elements having stable Electronic Configuration
	(b) By sharing of electrons (covalency)	Inert gases
All elements except inert gases	(c) By donation of at least a pair of electrons (Co-ordinate bonds or Dative bonds)	

(iv) The number of electrons which are involved in this chemical combination determine the valency of the element.

N. B. (a) *Electrovaleney*—Due to combination between metals and non-metals (Generally compounds are solids).

(b) *Covalency* : Due to combination between non-metals and non-metals (General).

Exception : $SnCl_4$, $AlCl_3$, $FeCl_3$, $HgCl_2$ etc. are covalent.

4.3. Electrovalency

Definition : *It is due to transference of electrons from the outermost orbit of one atom to the outermost orbit of another atom (dissimilar atom) till both acquired nearest inert gas configuration.* The element from which electrons are transferred becomes electropositive and which gained becomes electronegative. Thus electrostatic field is created between the two ions. Such bonds are also called *electrovalent, polar, electrostatic, ionic bond etc.* and the phenomenon is *called electrovalency.*

Examples : (i) **Formation of sodium chloride.**

Electronic configuration of sodium (*Na*) and chlorine (*Cl*) atoms are depicted in fig. 2.1.

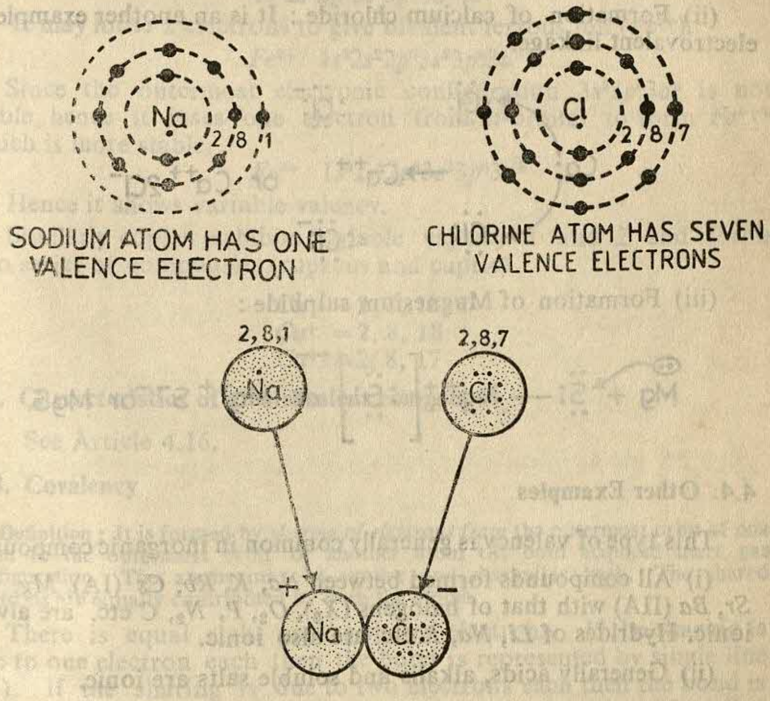

Na
2
8
1
Cl
2
8
7
SODIUM ATOM HAS ONE VALENCE ELECTRON
CHLORINE ATOM HAS SEVEN VALENCE ELECTRONS
2,8,1
2,8,7
Na
Cl
+
−
Na
Cl

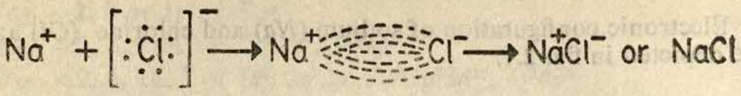
Fig. 2.1. Formation of Sodium Chloride

When sodium and chlorine atoms collide with each other, sodium atom loses its valency electron because of its low ionisation potential whereas the chlorine atom acquires this electron because the latter has high electron affinity and both of these atoms acquire stable configuration of Neon and Argon respectively. The sodium atom by losing its valency electron forms a positive ion (cation

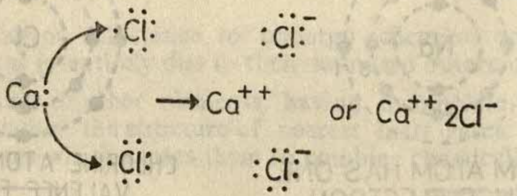
$$\underset{2,8,1}{Na} \longrightarrow \underset{2,8}{Na^+} + e^- \qquad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}\cdot + e^- \longrightarrow \underset{2,8,8}{\left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:\right]^-}$$

Na^+) and the chlorine atom by gaining that electron forms a negative ion (anion *Cl^-*). The ions are then held together by the electrostatic force of attraction between the ions thus formed.

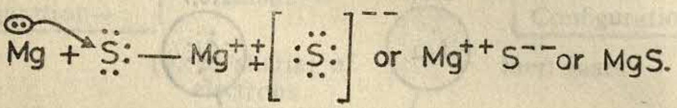
The formation of an ionic bond may be depicted as under :



(ii) Formation of calcium chloride : It is an another example of electrovalent linkage.



(iii) Formation of Magnesium sulphide :



4.4. Other Examples

This type of valency is generally common in inorganic compounds.

(i) All compounds formed between *Na*, *K*, *Rb*, *Cs* (IA), *Mg*, *Ca*, *Sr*, *Ba* (IIA) with that of halogens (X_2), O_2, *P*, N_2, *C* etc. are always ionic. Hydrides of *Li*, *Na*, *K* etc. are also ionic.

(ii) Generally acids, alkalis and soluble salts are ionic.

4.5. Conditions for the Formation of Ionic Bonds

The formation of ionic compound is favoured by (a) low ionisation energy of metal atom, (b) high electron affinity of non-metal atom, (c) the lattice energy of the compound formed should be high, (d) electrostatic force of attraction between ions should be high. According to Fajan's rule the electrovalency is favoured by (a) large cation, (b) small anion, (c) small charges on both anion and cation.

4.6. Variable electrovalency

There are many elements which show more than one electrovalency. This is generally found in the case of transition elements which have got inner core incomplete. The electronic configuration of transition element is

$$(n-1)d^{1-10}ns^2.$$

Since the energy difference between $(n-1)$ d and ns sub-shells is little, hence the electrons of these sub-shells take part in bond formation.

Example : The electronic configuration of iron (Fe) is

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$$

It may loose 2 electrons to give bivalent ferrous ion (Fe^{2+}).

$$Fe^{2+} \quad 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$$

Since the outermost electronic configuration $3s^2 3p^6 3d^6$ is not stable, hence it loses one electron from d-orbital to form Fe^{+++} which is more stable.

$$Fe^{3+} \quad 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$$

Hence it shows variable valency.

Similarly copper exhibits variable valency 1 and 2 and forms two series of compounds (cuprous and cupric)

$$Cu \;= 2, 8, 18, 1$$
$$Cu^{+} = 2, 8, 18$$
$$Cu^{++} = 2, 8, 17$$

4.7. Characteristics of etectrovalent compounds

See Article 4.16.

4.8. Covalency

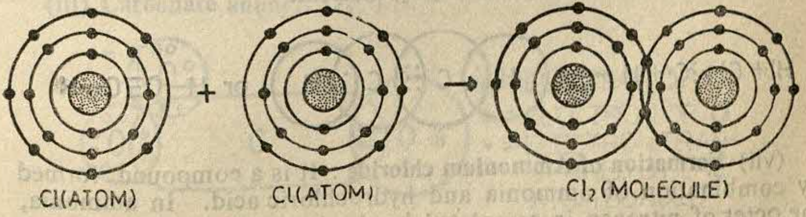
Definition : It is formed by *sharing of electrons from* the outermost orbit of one atom to the outermost orbit of another atom till both acquired inert gas configuration. The atoms may be similar and dissimilar both. The shared electrons are equally contributed by both the atoms.

There is equal right on the shared electrons. If the sharing is due to one electron each then the bond is represented by single line (—). If the sharing is due to two electrons each then the bond is represented by double line (=) and so on. Such bond is called covalent bond or non-polar or non-ionic bond.

Example : (I) Formation of chlorine (Cl_2) molecule :

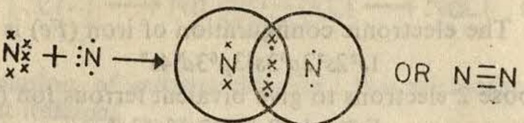
$$Cl(17) - 1s^2 2s^2 2p^6 3s^2 3p^5$$

Each chlorine atom acquires one electron to complete their octet. Hence each chlorine atom shares one electron to complete octet.

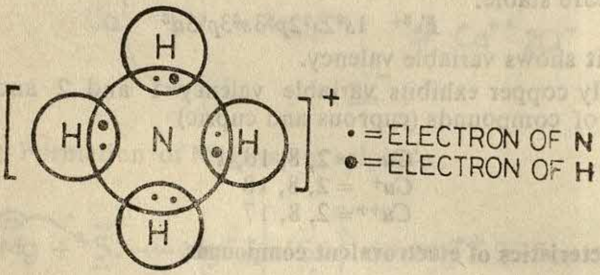


(ii) **Formation of Nitrogen (N_2) molecule :** Nitrogen atom has got

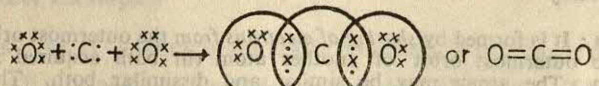
5 electrons in the outermost orbit. Hence nitrogen molecule is formed by sharing of three electrons by each nitrogen atom.



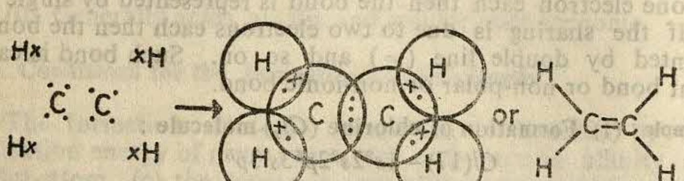
(iii) Formation of Ammonium ion :



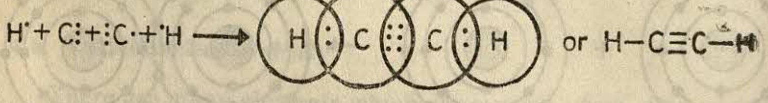
(iv) Formation of carbon dioxide molecule :



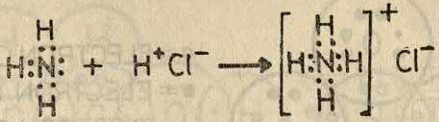
(v) Formation of ethylene (C_2H_4) molecule :



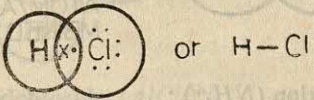
(vi) Formation of acetylene (C_2H_2) molecule :



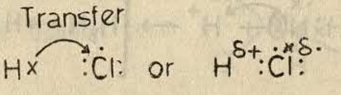
(vii) Formation of Ammonium chloride : It is a compound formed by combination of ammonia and hydrochloric acid. In ammonia, the octet of nitrogen is completed by sharing an electron each with three hydrogen atoms. The hydrogen ion of hydrochloric acid which has no electrons, accepts the lone pair of nitrogen to form ammonium ion which is linked to chlorine ion by electrovalency.



(viii) (a) **Hydrogen chloride** (*HCl* gas). It is a covalent compound.



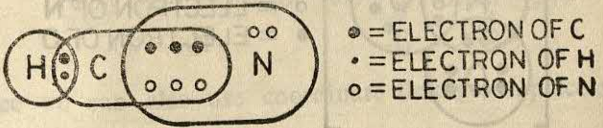
(b) **Hydrochloric acid** (*HCl* **acid**) : It is an ionic compound.



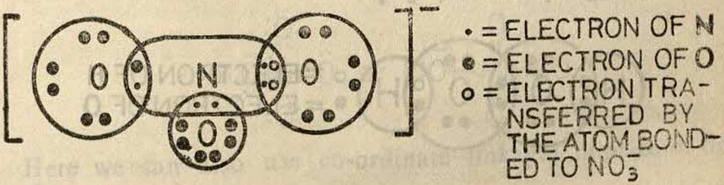
Hence *HCl* is a polar covalent.

4.9. Electron Dots Formulae of Some Important Compouuds

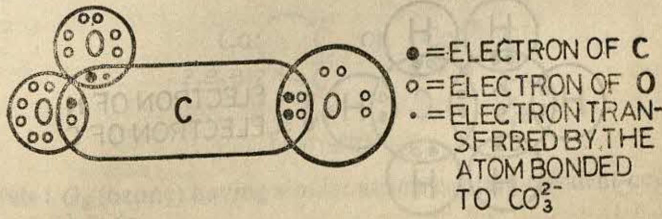
(i) **Hyrdogen cyanide** (*HCN*) :



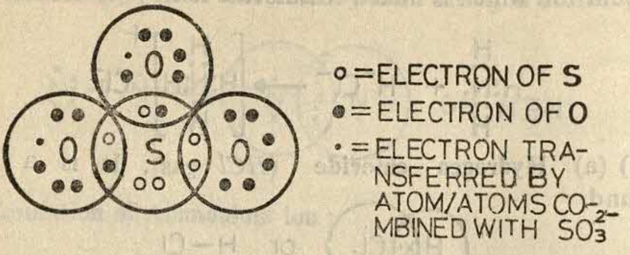
(ii) **Nitrate anion** (NO_3^{-1}) :



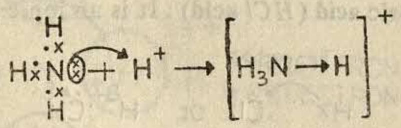
(iii) **Carbonate anion** (CO_3^{-2}) :



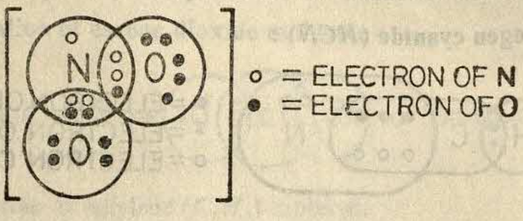
(iv) Sulphite anion (SO_3^{-2}) :


O
O
S
O
o = ELECTRON OF S
● = ELECTRON OF O
· = ELECTRON TRANSFERRED BY ATOM/ATOMS COMBINED WITH SO_3^{2-}

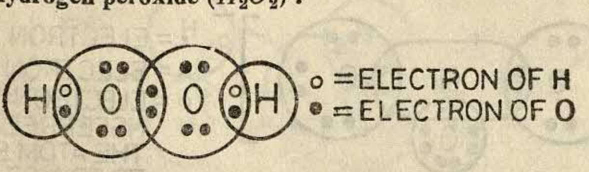
(v) Ammonium cation (NH_4^+) :



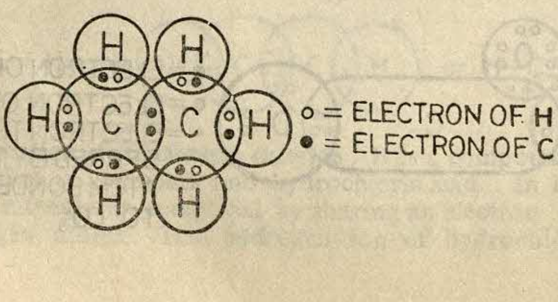
(vi) Nitrogen dioxide (NO_2) :



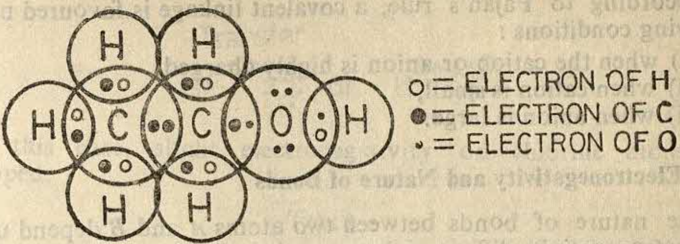
(vii) Hydrogen peroxide (H_2O_2) :



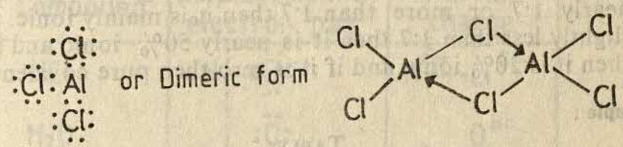
(viii) Ethane (C_2H_6) :



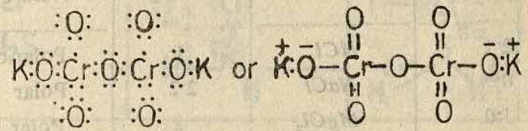
(ix) **Ethyl alcohol (C_2H_5OH) :**



(x) **Aluminium trichloride ($AlCl_3$) :**

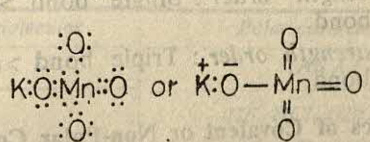


(xi) **Potassium dichromate ($K_2Cr_2O_7$) :**



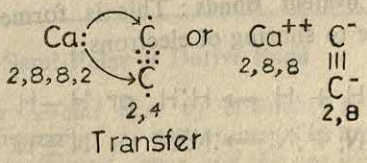
Hence we can also use coordinate linkages in place of double bonds.

(xii) **Potassium Permanganate ($KMnO_4$) :**



Here we can also use co-ordinate linkages in place of double bonds.

(xiii) Calcium Carbide (CaC_2) :



Note : O_3 (ozone) having similar atoms contain covalent-coordinate bonds.

4.10. Conditions for the Formation of Covalent Bonds

According to Fajan's rule, a covalent linkage is favoured under following conditions :

(i) when the cation or anion is highly charged,
(ii) when cation is small,
(iii) when anion is large.

4.11. Electronegativity and Nature of Bonds

The nature of bonds between two atoms *A* and *B* depend upon the electronegativity difference between the two atoms.

(i) If the electronegativity difference ($E_A - E_B$) between atoms is nearly 1·7 or more than 1·7 then it is mainly ionic. If it is slightly less than 1·7 then it is nearly 50% ionic and if it is 1 then it is 20% ionic and if it is zero then pure covalent.

Example :

TABLE

Element	*Edectronega-tivity*	*Molecule*	*E.N. diff.*	*Nature of bond*
H	2·1	HCl	1	Polar covalent
Na	0·9	$NaCl$	2·2	Polar
Mg	1·0	$MgCl_2$	2	Polar
Cl	3·1	Cl_2	0	Covalent

N.B. (1) Thus Hydrochloric acid is less polar and more covalent.

(2) *Bond length order* : Single bond > Double bond > Triple bond.

Bond strength order : Triple bond > Double Bond > Single bond.

4.12. Characteristics of Covalent or Non-Polar Compounds

See Article 4.16.

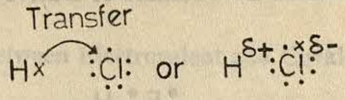
4.13. Types of Covalent Bonds

(i) **Non-polar Covalent Bonds** : This is formed between homo-nuclear atoms due to sharing of electrons.

$$H\cdot + \cdot H \longrightarrow H{:}H \text{ or } H{-}H$$

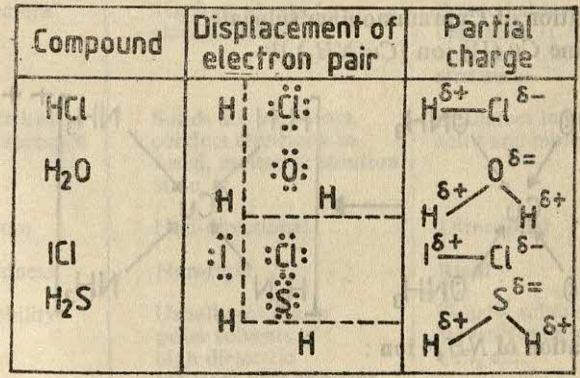
$$:\!\dot{N}\!: + :\!\dot{N}\!: \longrightarrow :\!N{\vdots}{\vdots}N\!: \text{ or } :\!N\equiv N\!:$$

(ii) **Polar Covalent Bonds** : There are some compounds such as HCl, H_2O, NH_3 etc. which are not purely covalent. This is due to more electronegativity of one element than other. Hence slight polarity is developed, as in *HCl*.



In this case, slight electronegativity on chlorine atom is developed.

TABLE



Compound	Displacement of electron pair	Partial charge
HCl	H : Cl :	$H^{\delta+}—Cl^{\delta-}$
H_2O	H :O: H	$H^{\delta+}$ $O^{\delta=}$ $H^{\delta+}$
ICl	:I: :Cl:	$I^{\delta+}—Cl^{\delta-}$
H_2S	H :S: H	$H^{\delta+}$ $S^{\delta=}$ $H^{\delta+}$

N. B. (1) Pure covalent (symmetrical) molecule has no dipole moment.

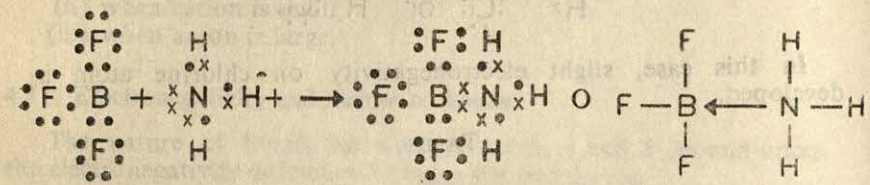
(2) TABLE

Non-polar covalent molecules	*Polar covalent molecules*
(*All X_2 type*)	(*All XY type*)
H_2, N_2, O_2, Cl_2 etc.	*HF, HCl, HBr, HI*
CH_4, C_2H_6, C_6H_6, C_2H_2, CCl_4	NH_3, PH_3 AsH_3
CO_2, BF_3, BCl_3, SO_3	H_2O, H_2S, SO_2, NO_2, N_2O,
	NO, *CO*, O_3, $CHCl_3$,
	ClF, ClBr, BrF

4.14. Co-ordinate or Semi-Polar or Dative Bond

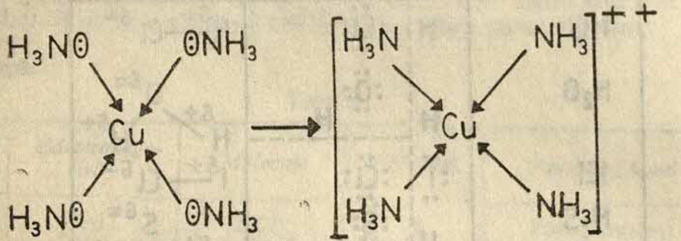
Definition : *It is a special case of covalency in which the pair of electrons is supplied by one of the two atoms. The atom which donates the pair of electrons is termed donor and the one which accepts those electrons is known as acceptor.* The donor must have capacity to donate at least a lone pair of electron and acceptor must have capacity to accept that. There is equal right on donated electrons. The bond is represented by arrow (→). It is from donor to acceptor side. Such bond is called Co-ordinate or Dative bond.

Example :

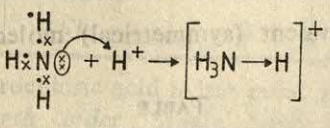


(2) Formation of Cuprammonium sulphate :

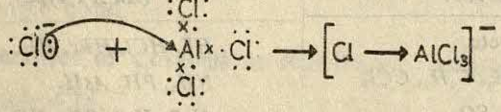
Tetrammine *Cu* (II) ion $[Cu(NH_3)_4]^{2+}$



(3) Formation of NH_4^+ ion :



(4) Formation of $AlCl_4^{-1}$ ion :



4.15. Characteristics of Co-ordinate Compounds

The properties of co-ordinate compounds are very much similar to those of covalent compounds in many respects.

(i) Once a co-ordinate covalent bond has been formed, there is no difference between it and a covalent bond. Therefore, like covalent compounds these compounds do not form ions in solutions or in the fused state and hence are poor conductors of electricity.

(ii) They are generally sparingly soluble in water. A number of them are largely soluble in organic solvents.

(iii) Like covalent bond, the co-ordinate covalent bond is rigid and directional, and therefore, such compounds also exhibit space isomerism.

4.16. Distinguish Between Electrovalent and Covalent Compounds

TABLE

Property	*Electrovalent or ionic*	*Covalent*
1. Structure	The ions always form giant structure	Bonded atoms form both molecular (CH_4, Cl_2 etc.) and giant (SiO_2, Diamond) structure
2. Electrical conductance	Solids are insulators, conduct electricity in fused, molten or solution state	Insulators in both solid and molten state
3. Nature	Non-directional	Directional
4. Rigidness	Non-rigid	Rigid
5. Solubility	Usually soluble in polar solvents of high dielectric constant such as water and insoluble in non-polar solvents	Usually soluble in non-polar solvents such as C_6H_6, CS_2, CCl_4 etc.
6. Melting and boiling point	High	Low
7. Rate of reactions	Usually fast since the ions have only to collide	Usually slow since the reaction generally involves bond breaking and bond making process
8. Space isomerism	Show no space isomerism	Show space isomerism
9. Electro-negativity	Electronegativity difference is larger	Electronegativity difference is less
10. I.P.	Between elements have low and high I.P.	Between elements have nearly same I.P.

4.17. Dipole Moment

When a bond is formed between two atoms that differ in electronegativity, there is an accumulation of negative charge on the more electronegative atom, leaving a positive charge on the more electropositive one.

The degree of polarity of a molecule is expressed in terms of dipole moments.

Definition : *It is defined as the product of the magnitude of the charge and distance between the two centres of charge; mathematically,*

$$\mu = e \times l$$

$$\underset{+e}{\bullet}\overset{}{\underset{l}{\rule{3cm}{0.4pt}}}\underset{-e}{\bullet}$$

Dipole moment $\mu = e \times l$

where e = electronic charge = $4{\cdot}8 \times 10^{-10}$ esu or $1{\cdot}6 \times 10^{-19}$ coulomb.

l = distance between the two centre of charge is always in the order of 10^{-8} cm or 10^{-10} metre.

Unit of dipole moment $\mu = e \times l = 4{\cdot}8 \times 10^{-10}$ esu $\times 10^{-8}$ cm
$= 4{\cdot}8 \times 10^{-18}$ esu cm $= 4{\cdot}8$ D (1 D $= 10^{-18}$ esu cm)
(I D = Debye)

In S.I. unit $= 10^{-19}$ coulomb $\times 10^{-10}$ metre $= 10^{-29}$ coulomb-metre.

The dipole moment is a vector quantity directed from positive to the negative charge, e.g.

Representation : $H \longrightarrow F$

Applications of Dipole Moment :

(i) Estimation of the extent of ionic character in a bond,

for HCl; $H \overset{l}{\text{———}} Cl$, $l = 1{\cdot}275\,\mathring{A} = 1{\cdot}275 \times 10^{-8}$ cm
$e = 4{\cdot}802 \times 10^{-10}$ esu
(Theoretically) $\mu = e \times l = 4{\cdot}802 \times 10^{-10} \times 1{\cdot}275 \times 10^{-8}$ esu cm
$= 6{\cdot}11 \times 10^{-18}$ esu cm $= 6{\cdot}11$ D

Experimentally μ for $HCl = 1{\cdot}03$ D

$$\%\text{ of ionic character} = \frac{\mu_{obs}}{\mu_{cal}} \times 100 = \frac{1{\cdot}03}{6{\cdot}11} \times 100 = 17\%$$

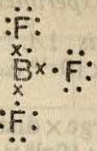
Thus HCl ($\mu = 1{\cdot}03$ D) is more polar than HBr ($\mu = 0{\cdot}79$ D)

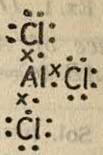
The symmetrical molecule (like linear, regular corner of a tetrahedron or planar triangular structure or a planar hexgonal structure) has zero dipole moment. In such molecules, the dipoles developed in opposite directions cancel out.

Example : (a) Linear symmetrical molecule ($\mu = 0$) :
$O=C=O$, $S=C=S$, $H-C\equiv C-H$, $H-H$ etc.

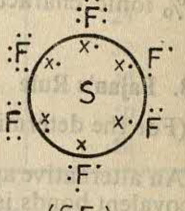
(b) Tetrahedral molecule ($\mu = 0$) :
CCl_4, $SnCl_4$, CH_4

(c) Planar triangular molecule ($\mu = 0$) :





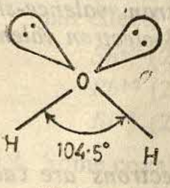
(d) Planar hexagonal molecule ($\mu = 0$) :



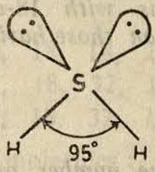
(SF_6)

(2) **Deciding the geometry of polar molecules :**

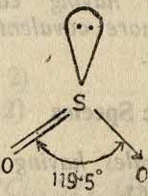
Water ($\mu = 1{\cdot}84$ D), H_2S ($\mu = 0{\cdot}95$ D), SO_2 ($\mu = 1{\cdot}61$ D) NH_3 ($\mu = 1{\cdot}47$ D) have assigned angular structure instead of linear structures, as shown :



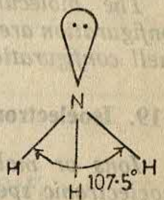
WATER



HYDROGEN SULFIDE



SULPHER DIOXIDE

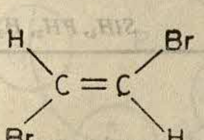


AMMONIA

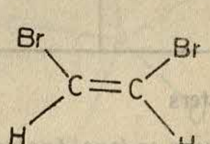
(3) **Cis-trans isomer can be distinguished by dipole moment.**

The trans compounds will have a negligible dipole moment ($\mu = 0$) due to the cancellation of the individual bond moments, but the cis isomer will have a definite dipole moment.

Example :



Trans dibromoethane
($\mu = 0$)



Cis dibromoethane
($\mu = 1{\cdot}35$ D)

Ex. 1. *The experimental dipole moment of A-B is* 1·3 *D. The distance of A-B is* $1\mathring{A}$. *Calculate the percentage ionic character of AB.* ($e = 4{\cdot}8 \times 10^{-10}$ *e.s.u.*)

Sol. $\mu = \text{charge} \times \text{distance}$
$= 4{\cdot}8 \times 10^{-10} \times 10^{-8} = 4{\cdot}8 \times 10^{-18} = 4{\cdot}8\ \text{D}$ $[1\mathring{A} = 10^{-8}\ \text{cm}]$

$$\%\ \text{ionic character} = \frac{\text{Experimental } \mu}{\text{Calculated } \mu} \times 100 = \frac{1{\cdot}3}{4{\cdot}8} \times 100 = 27{\cdot}08.$$

4.18. Fajan's Rule

(For the determination of ionic or covalent character)

An alternative approach to explain the formation of either ionic or covalent bonds is provided by the Fajan's Rules.

The rules can be summarised by saying that the molecules containing (a) high positive charge on the cation, (b) high negative charge on the anion, (c) small cation or large anion are covalent in character while those containing (a) low positive charge on the cation, (b) low negative charge on the anion, (c) large cation or small anion show ionic character.

The molecules having cations with 18-electron valence-shell configuration are more covalent than those having 8-electron valence-shell configuration.

4.19. Isoelectronic Species

Ions or molecules having same number of electrons are called isoelectronic species.

TABLE

Number of electrons	*Isoelectronic with*	*Examples*
10	Neon	$Na^{+}, Mg^{+2}, Al^{+3}, N^{-3}, O^{-2}, F^{-1}$, CH_4, NH_3, H_2O, HF
18	Argon	$K^{+}, Ca^{+2}, Sc^{+3}, Tl^{+4}, P^{-3}, S^{-2}, Cl^{-}$ SiH_4, PH_3, H_2S, HCl

4.20. Isosters

Molecules or ions (polyatomic) containing the same number of atoms and the same total number of electrons are called isosters. Isosters show similar structural properties.

TABLE

Isosteric species	*No. of atoms*	*No. of electrons*
N_2, CO, CN^-, NO^+	2	14
CH_4, NH_4^+	5	10
CO_2, N_2O, N_3^{-1}, CNO^{-1}, NO_2^+	3	22
O_3, NO_2^{-1}	3	24
NO_3^{-1}. CO_3^{-2}, BO_3^{-3}	4	32
ClO_3^{-1}, SO_3^{-2}	4	42
ClO_4^{-1}, PO_4^{-3}	5	50
MnO_4^{-1}, CrO_4^{-2}	5	58

4.21. Species Which Do Not Follow The Octet Rule

1. Cations of some transition metals, having 18 electrons in their outermost shell :

   Cu^+ (2, 8, 18); Zn^{+2} (2, 8, 18)
   Ag^+ (2, 8, 18, 18); Hg^{+2} (2, 8, 18, 32, 18)

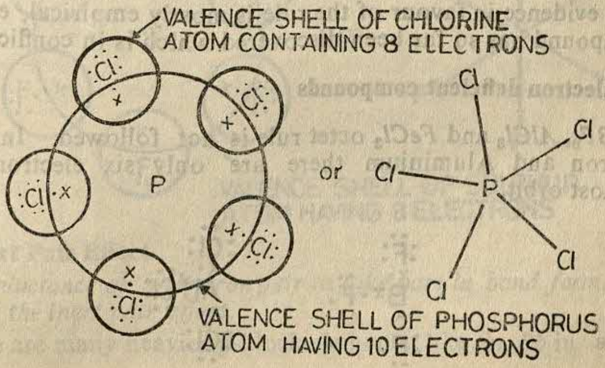
2. Cations having 2 electrons in their outermost shell (**due to inert pair effect**) :

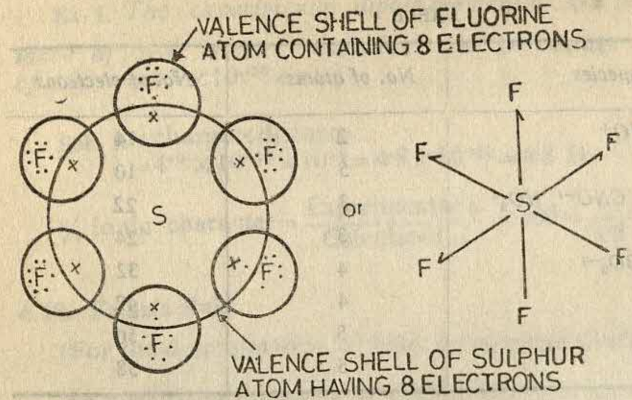
   Sn^{+2} (2, 8, 18, 18, 2)
   Pb^{+2} (2, 8, 18, 32, 18, 2)
   Bi^{+3} (2, 8, 18. 32, 18, 2)

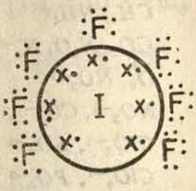
3. Some covalent molecules :

   O_2, $BeCl_2$, BF_3, NO, NO_2, PCl_5, SF_6, IF_7, OsF_8

Octet rule cannot explain the formation of PCl_5, SF_6, IF_7. In these compounds, the total number of electrons in the outermost orbit of P, S and I are 10, 12 and 14 respectively


VALENCE SHELL OF CHLORINE
ATOM CONTAINING 8 ELECTRONS
P
or
Cl
Cl
Cl
P
Cl
Cl
VALENCE SHELL OF PHOSPHORUS
ATOM HAVING 10 ELECTRONS


VALENCE SHELL OF FLUORINE ATOM CONTAINING 8 ELECTRONS
S
or
F
S
VALENCE SHELL OF SULPHUR ATOM HAVING 8 ELECTRONS



(IF_7)

4.22. Sidgwick's Covalency Rule (Maximum Covalency)

There is in fact a definte limit to the covalency of an element. Each element has a covalency maximum. Sidgwick gave a rule regarding maximum covalency of an element according to which

"The maximum covalency of an element is limited according to its period in the periodic table, being 2 for hydrogen, 4 for the elements of the second period (*Li* to *F*), 6 for those of the third and fourth period and for all the rest 8."

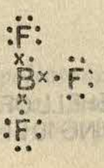
TABLE

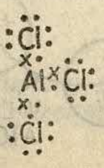
Atomic Number	*Element*	*Maximum Covalency*	*Maximum electrons in sharing*
1	*H*	1	2
3—9	*Li—F*	4	8
11—35	*Na—Br*	6	12
37—92	*Rb—U*	8	16

The evidence in favour of the rule is mostly empirical, even then no compound has so far been discovered which is in conflict with it.

4.23. Electron deficient compounds

In BF_3, $AlCl_3$ and $FeCl_3$ octet rule is not followed. In the case of Boron and Aluminium there are only six electrons in their outermost orbit.

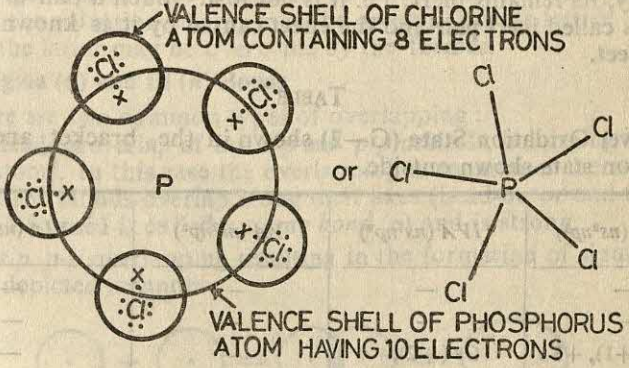




According to octet rule, these compounds should not be stable but they are most stable. They are known as *Lewis Bases.*

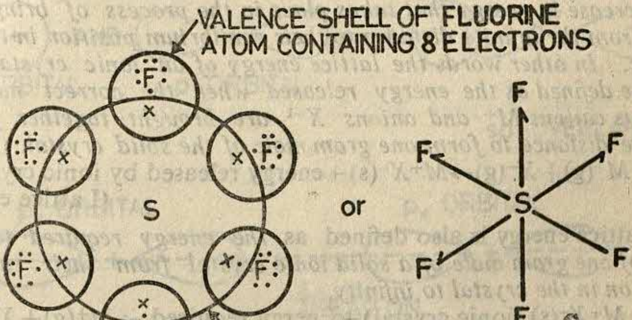
4.24. One Electron Bond (Singlet Bond)

(i) Phosphorus Pentachloride : Formerly it was believed that in the formation of PCl_5 the maxima of 8 electrons in the valency shell are excceded to 10 so that the number ,of electrons round phosphorus are 10 (Formula I).


VALENCE SHELL OF CHLORINE ATOM CONTAINING 8 ELECTRONS
Cl
Cl
Cl
Cl
Cl
P
or
Cl
Cl
P
Cl
Cl
Cl
VALENCE SHELL OF PHOSPHORUS ATOM HAVING 10 ELECTRONS

But according to **Sugden** the valency maxima cannot excced eight and some of the chlorine atoms in PCl_5 are joined to phosphorus by singlet i.e. formed by sharing of single electron only (Formula II).

(ii) Sulphur Hexafluoride ;


VALENCE SHELL OF FLUORINE ATOM CONTAINING 8 ELECTRONS
F
F
F
F
F
F
S
or
F
F
F
S
F
F
F
VALENCE SHELL OF SULPHUR ATOM HAVING 8 ELECTRONS

4.25. Inert Pair Effect

The reluctance of s-electron pair to take part in bond formation is known as the inert pair effect.

There are many heavier p-block elements, like *Sn, Pb* in addition to their group *G* (oxidation state), also exhibit lower oxidation states equal to (G-2). *Examples* of such elements are given in table given below.

Group number *G* is obtained when all the *ns* and *np* electrons from ns^2p^x configuration of p-block elements ($x = 1, 2, 3$ and 4 for the elements of group IIIA, IVA, VA and VIA respectively) are lost, while the lower oxidation state equal to (G-2) is obtained when only *np*-electrons are lost and the *ns*-electron pair, due to its extra stability, its remains inert, i.e. it is not lost. Such a pair of *ns*-electrons is called **inert pair** and the effect caused by it is known as **inert pair effect.**

TABLE

Lower Oxidation State (G—2) shown in the bracket and group oxidation state shown outside.

IIIA (ns^2np^1)	*IVA* (ns^2np^2)	*VA* (ns^2np^3)	*VIA* (ns^2np^4)
—	—	—	—
—	—	—	—
Ga (+1), +3	*Ge* (+2),+4	—	—
In (+1),+3	*Sn* (+2),+4	*Sb* (+3),+5	*Te* (+4),+6
Tl (+1),+3	*Pb* (+2),+4	*Bi* (+3),+5	*Po* (+2),+6

4.26. Lattice Energy of Ionic Crystals

Definition : *The lattice energy of an ionic crystal may be defined as the decrease in energy that takes place in the process of bringing the ions from the infinite distance to their equilbrium position in the stable lattice. In other words the lattice energy of an ionic crystal* M^+X^- *may be defined as the energy released when the correct number of gaseous cations* M^+ *and anions* X^{-1} *are brought together from an infinite distance to form one gram mole of the solid crystal.*

$M^+(g) + X^-(g) \rightarrow M^+X^-(s) +$ energy released by ionic crystal (Lattice energy, U)

Lattice energy is also defined as *the energy required to remove ions of one gram mole of a solid ionic crystal from their equilibrium position in the crystal to infinity.*

$M^+X^-(s)$ (ionic crystal) + Energy required $\rightarrow M^+(g) + X^-(g)$

Hence the lattice energy is the same in magnitude but opposite in sign to the energy of dissociation of the crystal. It follows, therefore, that greater the value of lattice energy, numerically, the greater is the energy required to decompose the ionic crystal M^+X^- into its constituent ions, M^+ and X^-.

Application of Lattice Energy : With the help of lattice energy we can estimate electron affinites, proton affinites, and heats of formation.

Further applications are found

(a) in the derivation of crystal field stabilisation energies.

(b) to account the stabilities of metal hydrides, polyhalides, and peroxides and super oxides.

(c) as the discussion of the special properties of fluorine in relation to other halogens.

Relation Between Lattice Energy and Solubility of Ionic solids :

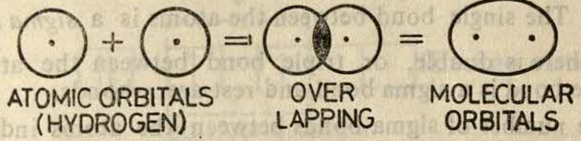
As a general rule for a solid to be able to dissolve in a particular solvent, the solvation energy must be greater than its lattice energy, so that the latter may be overcome by the former.

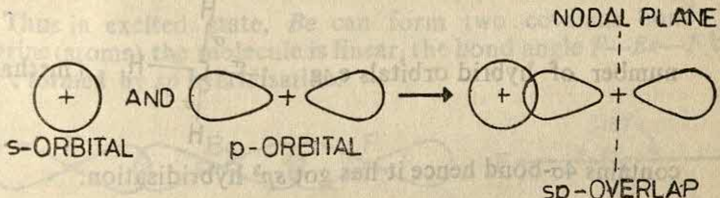
4.27. Sigma (σ) and Pi (π) Bonds

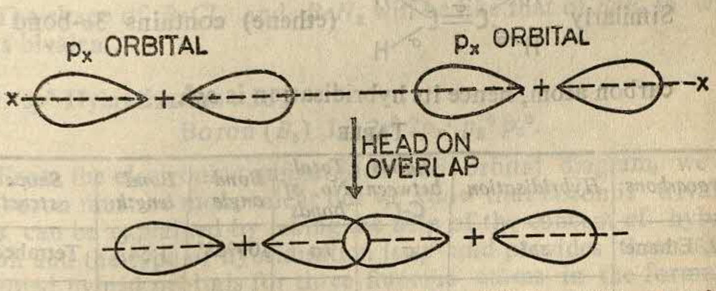
There are two common types of overlapping :

(i) **Head-on overlap of** ***s-s*****,** ***s-p*** **and** ***p-p*** **orbitals**, belonging to combining atoms. In this case the overlapping is maximum because the two electron clouds overlap along their axes (head-on or end-to-end). The bond formed is called a *sigma bond* (σ) and is strong.

s-s, *s-p*, *p-p* overlapping resulting in the formation of sigma bond may be depicted as under :

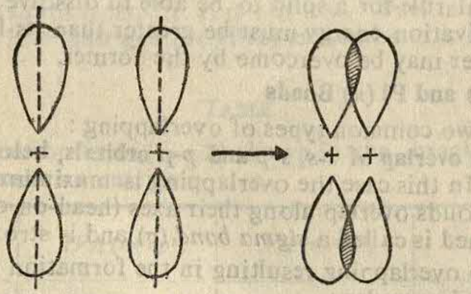






(ii) **Sidewise or lateral overlapping of p-orbitals** : When a sigma bond is formed between *s-p* or p_x-p_x overlapping, the other *p* orbital namely p_y and p_y orbitals may have unpaired electrons. These orbitals are at right angle to the sigma bond formed by the head-on co-axial overlapping. Only lateral or sidewise overlapping of p_y and p_z orbitals can now take place. The lateral overlapping can take place only to a small extent and bond formed is referred to as *pi-bond* (π-bond). This type of bond is comparatively a much weaker bond.

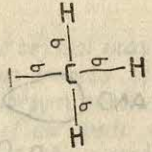
The formation of pi-bond may be depicted below :

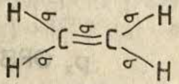


TWO p ORBITALS SIDE-WISE OVERLAP

N.B. (a) The single bond between the atoms is a *sigma bond.*

(b) If there is double, or triple bond between the atoms then one bond is a sigma bond and rest are π-bonds.

(c) The number of sigma bonds between the atoms indicate the number of hybrid orbitals e.g  (methane) contains 4σ-bond hence it has got sp^3 hybridisation.

Similarly  (ethene) contains 3σ-bond per carbon atom, hence its hybridisation is sp^2.

TABLE

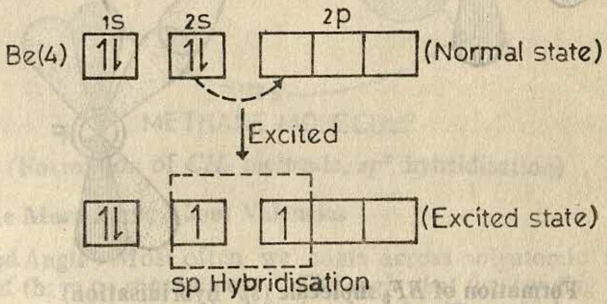
Hydrocarbons	*Hybridisation*	*Bonds between C-C*	*Total No. of bonds*	*Bond angle*	*Bond length*	*Shape and structure*
C_2H_6 Ethane	sp^2	σ	7σ	109°28′	1·54Å	Tetrahedral
C_2H_4 Ethene	sp^2	1σ, 1π	5σ, 1π	120°	1·34Å	Angular
C_2H_2 Ethyne	sp	1σ, 2π	3σ, 2π	180°	1·20Å	Linear

4.28. Hybridisation

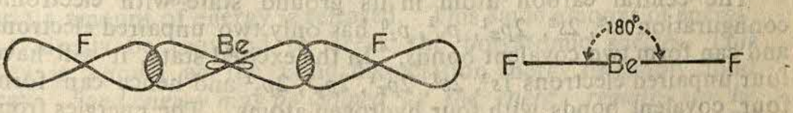
Definition : *The process of redistribution of energy amongst the orbitals of different energy so as to produce orbitals of equivalent energy is known as hybridisation. For example*, mixing one '*s*' and one '*p*' orbital in an atom gives two equivalent *sp* hybrid orbitals. Stronger bonds are formed by hybridisation than with pure atomic orbitals.

4.29. *sp* Hybridisation : BeF_2

Be atom in its ground state with the electronic configuration $1s^2$, $2s^2$ has no unpaired electrons but in excited state it has two unpaired electrons.



Thus in excited state, *Be* can form two covalant bonds with fluorine (atoms) the molecule is linear, the bond angle *F—Be—F* being 180°, **formed by *sp* hybridisation.**



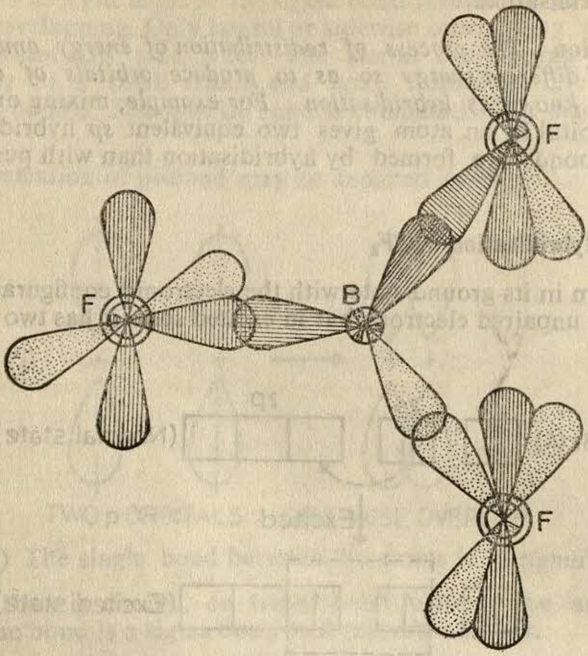
The shape of $BeCl_2$ and BeH_2 will be like that of BeF_2 in which *Be* is bivalent.

4.30. sp^2 Hybridisation : BF_3

Boron (B_5) $1s^2\ 2s^2\ 2p_x^1\ p_y^0\ p_z^0$.

From the electronic configuration and orbital diagram, we can say boron must be monovalent but we know that boron is trivalent. This can be explained by taking the help of the concept of hybridisation and the type of hybridisation is sp^2 and provides three singly occupied hybrid orbitals for three fluorine atoms in the formation of BF_3.

B(5) Ground state $1s^3 2s^2 2p_x^1 p_y^0 p_z^0$
Excited state $1s^2 2s^1\ 2p_x^1 p_y^1 p_z^0$



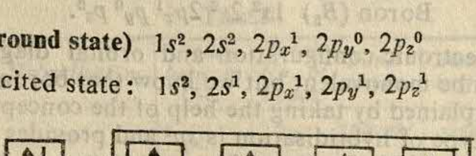
Formation of BF_3 molecule (sp^3 hybridisation)

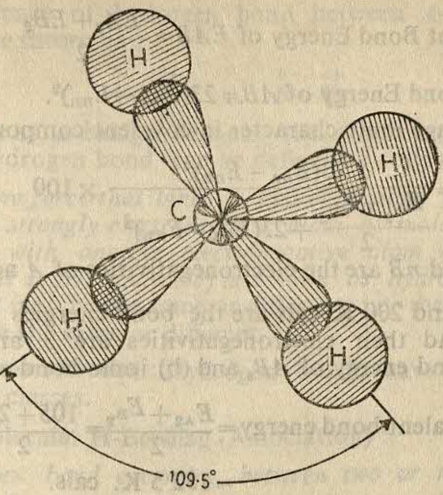
4.31. sp^3 hybridisation : CH_4, CCl_4, NH_4^+, H_3O^+

The central carbon atom in its ground state with electronic configuration $1s^2$, $2s^2$, $2p_x^1$, p_y^1, p_z^0 has only two unpaired electrons and can form two covalent bonds. In the excited state, it will have four unpaired electrons $1s^2$, $2s^1$, $2p_x^1$, $2p_y^1$, $2p_z^1$ and hence can form four covalent bonds with four hydrogen atoms. The energies from four unpaired orbitals (2s and three 2p) are pulled and four equivalent sp^3 hybrid orbitals are formed. Thus CH_4 or CCl_4 molecule have tetrahedral structure with carban atom at the centre of tetrahedron and four hydrogen atoms at the corners, making a bond of 129°28′.

Carbon (**Ground state**) $1s^2$, $2s^2$, $2p_x^1$, $2p_y^0$, $2p_z^0$

Excited state : $1s^2$, $2s^1$, $2p_x^1$, $2p_y^1$, $2p_z^1$





METHANE MOLECULE

(Formation of CH_4 molecule, sp^3 hybridisation)

4.32. Some More Facts About Valencies

(i) Bond Angle : Most often we come across polyatomic species made up of three or more atoms. *The angle that two bonding atoms make at a central atom is called the bond angle.* Thus the bond angle in H_2O is 105°. This means that the angle formed by the two $H-O$ bonds at the oxygen atom is 105°.

(ii) Bond Energy : When atoms interact to give polyatomic species a certain amount of energy is released. This same amount of energy, will evidently be required to break the polyatomic species. This energy is known as the bond dissociation energy or simply bond energy. *Bond energy may be defined as the energy required to be supplied to the molecule (or polyatomic species) to break the bond in the gaseous state i.e. to take the interacting atoms to infinity.* Bond energy of H_2 molecules is 104 K cal/mole. This means 104 K cal/mole of energy has to be supplied to one gm mole of hydrogen in order to separate the interacting hydrogen atoms. *Larger the bond energy, the stronger is the bond.* The single bond has lowest bond energy, the doudle bond has nearly two times that of single bond and triple bond has higher bond energy than double bond.

(iii) Bond Length : *It is the average internuclear distance between two atoms in a molecule.* (The term 'average' has been used because the bonded atoms are always vibrating so that the distance between the atoms is not fixed for all time—but an average distance can be determined by modern experimental technique.) The bond lengths of Cl_2 and I_2 are 1·98 and 2·66Å respectively.

(iv) Covalent Bond Energy of $EAB = \dfrac{EA_2 + EB_2}{2}$.

(v) Ionic Bond Energy of $AB = 23(E_{nA} - E_{nB})^2$.

(vi) Percentage ionic character in covalent compound

$$= \frac{23(E_{nA} - E_{nB})^2}{\dfrac{E_{A_2} + E_{B_2}}{2} + 23(E_{nA} - E_{nB})^2} \times 100$$

where nA and nB are the electronegativities of A and B.

Ex. 2. 105 and 200 K cals are the bond energies of A_2 and B_2 respectively, and their electronegativities are 3 and 4. Calculate (a) covalent bond energy of AB, and (b) ionic bond energy of AB.

Sol. (a) Covalent bond energy $= \dfrac{E_{A2} + E_{B_2}}{2} = \dfrac{105 + 200}{2}$

$= 152{\cdot}5$ K. cals.

(b) Ionic bond energy $= 23(E_{nA} - E_{nB})^2 = 23(3-4)^2 = 23$ K. cals.

Ex. 3. 100 and 200 K. cals. are the bond energies of X_2 and Z_2 respectively, and their electronegativities are 3 and 4. Calculate the percentage of ionic character of XZ.

Sol. $EX_2 = 100$, $EZ_2 = 200$; $E_nX = 3$, $E_nZ = 4$.

$$\% \text{ of ionic character of } XZ = \frac{23(E_nX - E_nZ)^2}{\dfrac{EX_2 + EZ_2}{2} + 23(E_nX - E_nZ)^2} \times 100$$

$$= \frac{23+1}{\dfrac{100+200}{2} + 23(3-4)^2} \times 100 = \frac{23}{173} \times 100 = 13{\cdot}29\%.$$

4.33. Hydrogen Bond

In order to understand the concept of hydrogen bond let us consider a molecule. Say, HA in which H atom is linked with a strongly electronegative atom A (A may be N, O or F) by a normal covalent bond. The electron pair being shared between H and the strongly electronegative atom A will evidently lie far away from H atom and thus partial positive and negative charges will be developed on H and A atoms respectively. Consequently HA molecule will behave as a dipole represented as $H^{\delta+}—A^{\delta-}$ with A as its negative and H as its positive end. If another molecule $H—B$ which also forms a dipole $H^{\delta+}—B^{\delta-}$ (B is a strongly electronegative atom like N, O and F) is brought near $H—A$ dipole, these two dipoles will be linked together by a special type of bond which is called **hydrogen bond** and is *represented by dotted lines.*

Thus the existence of hydrogen bond between $A—H$ and $B—H$ molecules can be shown as :

$$\overset{\delta-}{A}—\overset{\delta+}{H}\ldots\ldots\ldots\overset{\delta-}{B}—\overset{\delta+}{H}$$

H-atom acts as a bridge between the electronegative atoms, A and B. Thus hydrogen bond can be defined as follows :

The attractive force that binds a hydrogen atom which is already attached with a strongly electronegative atom of molecule (here it is HA molecule) with another electronegative atom of some other molecule (here it is BH molecule) is known as hydrogen bond. The atoms A and B may be the same or different, i.e. the molecules AH and BH may be the same or different.

Types of Hydrogen Bonding : Hydrogen bonds have been classified into two major classes.

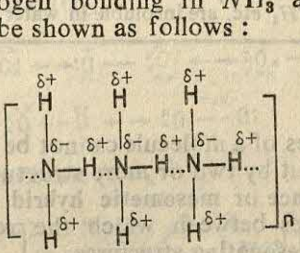
(a) **Inter-molecular H-Bonding** (Association) :

The hydrogen bond occurring between two or more similar or different molecules is called inter-molecular hydrogen bonding.

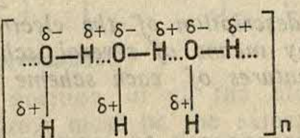
Examples : (i) H_2O, NH_3 and HF molecules : When a number of HF molecules are brought together, the positive end of one dipole $H^{\delta+}—F^{\delta-}$ attracts the negative end of the other similar dipole, $H^{\delta+}—F^{\delta-}$ and these molecules are *associated* together to form a cluster $(HF)_n$ shown as :

$$\left[\ldots\overset{\delta+}{H}—\overset{\delta-}{F}\ldots\overset{\delta+}{H}—\overset{\delta+}{F}\ldots\overset{\delta+}{H}—\overset{\delta+}{F}\ldots\overset{\delta+}{H}—\overset{\delta-}{F}\ldots\right]_n$$

The formation of the associated molecules of the hydrides of N and O viz. $(NH_3)_n$ and $(H_2O)_n$ is due to the existence of their inter-molecular hydrogen bonding in NH_3 and H_2O molecules. Their formation can be shown as follows :



$$\left[\begin{array}{llllll} \overset{\delta+}{H} & & \overset{\delta+}{H} & & \overset{\delta+}{H} & \\ | & & | & & | & \\ \ldots\overset{\delta-}{N} & —\overset{\delta+}{H}\ldots & \overset{\delta-}{N} & —\overset{\delta+}{H}\ldots & \overset{\delta-}{N} & —\overset{\delta+}{H}\ldots \\ | & & | & & | & \\ H^{\delta+} & & H^{\delta+} & & H^{\delta+} & \end{array}\right]_n$$



$$\left[\begin{array}{llllll} \ldots\overset{\delta-}{O} & —\overset{\delta+}{H}\ldots & \overset{\delta-}{O} & —\overset{\delta+}{H}\ldots & \overset{\delta-}{O} & —\overset{\delta+}{H}\ldots \\ \delta+| & & \delta+| & & \delta+| & \\ H & & H & & H & \end{array}\right]_n$$

Intra-molecular *H*-bonding (Chelation) : *Hydrogen bonding occurring* *within a single molecule is called intra-molecular H-bonding.* In intramolecular *H*-bonding the *H*-atom is bonded to two atoms of the same molecules. This type of *H*-bonding may lead to the linking of two groups to form a ring structure.

Examples: Ortho-nitrophenol, ortho-hydroxybenzaledehyde, salicylic acid etc.

Properties of Hydrogen Bond : (i) A *H*—bond is a bond of hydrogen between two electronegative atoms only. It never involves more than two atoms (excluding *H*-atoms).

(ii) Bond energy of a *H*-bond is in the range of 3 to 10 k cal/mole while that of a normal covalent bond is in the range of 50 to 100 k cal/mole Thus a *H*-bond (i.e. $H \ldots\ldots B$ bond) is much weaker than a covalent bond, $A—H$.

(iii) The formation of a *H*-bond does not involve any sharing of electron pairs. It is therefore, quite different from a covalent bond.

(iv) Compounds containing hydrogen bond have high melting and boiling point. They are generally soluble in water.

TABLE

Terms	*Nature and Boiling point*
Compounds having *H*-bond	H_2O (*l*, high b. p.), HF (*l*, high b.p.), NH_3 (g)(high b.p), CH_3OH (*l*) All are soluble in water.
Compounds having no *H*-bond	H_2S (g, low b.p.) HI (g, low b.p.), PH_3 (g, low b.p.) CH_4 (g, low b.p.). PH_3, CH_4 etc. are insoluble in water.

4.34. Resonance

When the properties of a molecule cannot be completely described by a single structure but by two or more structures, its true structure is said to be a **resonance** or **mesomeric hybrid** of these structures. These various structures between which the resonance occurs are called **contributing** or **resonating structures**.

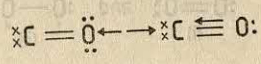
Resonance is the description of the electronic structures of a molecule or an ion by means of several schemes of pairing of electrons, with the features of each scheme contributing in the description

The effect of a resonance is to increase the stability of the molecule in which it occurs.

The increase in stabiity resulting from the resonance explains bond lengths, heats of reaction and the rates of chemical reactions.

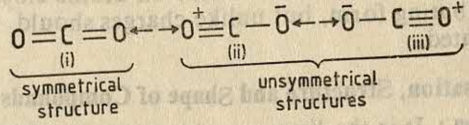
Resonance Structures of Some Species :

(i) Carbon monoxide molecule (*CO*) :



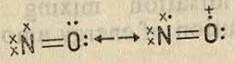
$$\overset{\times}{_\times}C=\underset{\cdot\cdot}{\ddot{O}} \longleftrightarrow \overset{\times}{_\times}C\equiv O:$$

(ii) Carbon dioxide molecule (CO_2) :



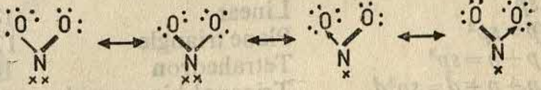
$$\underbrace{\underset{(i)}{O=C=O}}_{\text{symmetrical structure}} \longleftrightarrow \underbrace{\underset{(ii)}{\overset{+}{O}\equiv C-\bar{O}} \longleftrightarrow \underset{(iii)}{\bar{O}-C\equiv O^{+}}}_{\text{unsymmetrical structures}}$$

(iii) Nitric oxide molecule (*NO*) :

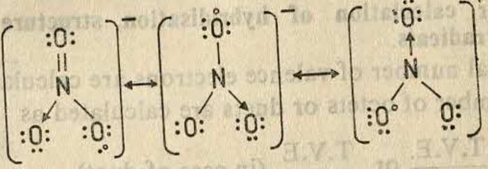


$$\overset{\times}{_\times}\overset{\times}{N}=\ddot{O}: \longleftrightarrow \overset{\times}{_\times}\overset{\times\cdot}{N}=\overset{+}{\ddot{O}}:$$

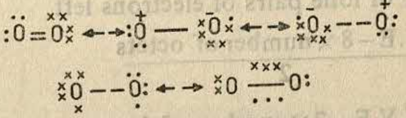
(iv) Nitrogen dioxide molecule (NO_2) :



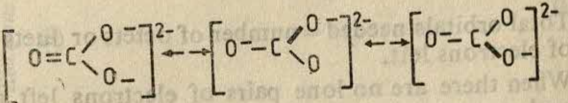
(v) Nitrate ion (NO_3^{-1}) :



(vi) Oxygen molecule (O_2) :



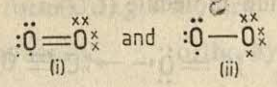
(vii) Carbonate molecule (CO_3^{-2}) :



The conditions of resonance :

(i) The relative position of all the atoms in each of the resonance forms must be the same; the arrangement of electron may differ.

(ii) The number of unpaired and paired electrons in each of the resonance forms must be the same so that a continuous change from one bond type to another type may occur. For example,



(iii) Contributing srtructures should be of equal energy.

(iv) Like charges should not reside on atoms close together in a contributing form, but unlike charges should not be greatly separated.

4.35. Hybridisation, Structure and Shape of Compounds and Radicals

Hybridisation : It is the linear combination of different atomic orbitals in the same atom to give same number of equivalent atomic orbitals. In the hybridisation mixing of orbitals take place through which redistribution of energy among different orbitals take place e.g.,

Hybridisation	**Structure**	**Bond Angle**
$s+p=sp$	Linear	180°
$s+p+p=sp^2$	Plane triangle	120°
$s+p+p+p=sp^3$	Tetrahedron	109°28′
$s+p+p+p+d=sp^3d$	Trigonal bipyramid	120° and 90°
$s+p+p+p+d+d=sp^3d^2$	Octahedron	90°

Rules for calculation of hybridisation, structure and shape of molecules or radicals.

(i) Total number of valence electrons are calculated = T. V. E.

(ii) Number of octets or duets are calculated as

$$=\frac{\text{T.V.E.}}{8} \text{ or } \frac{\text{T.V.E}}{2} \text{ (in case of duet).}$$

(iii) Number of lone pairs of electrons left

$$=\frac{\text{T.V.E}-8\times\text{number of octets}}{2}$$

$$\text{or } \frac{\text{T.V.E}-2\times\text{number of duets}}{2}.$$

(iv) Total orbitals needed = number of octets or duets + lone pair of electrons left.

(v) When there are no lone pairs of electrons left then shape and structures are the same.

(vi) When there will be lone pairs of electrons left then shape will be different than structure.

For full explanation and calculation follow Table.

4.36. How to Find Out Hybridisation

TABLE

Molecule (i)	Total Valency Electrons (ii)	Total no. of bonds (iii)	Electrons for Duet or Octet (iv)	No. of Lone pair of electrons left $\frac{(ii)-(iv)}{2}$ (v)	No. of orbitals (iii)+(v)	Hybridisation	Structure	Shape

Note :

(ii) Td $(H_2O)_n$
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(i) There is no hybridisation in H_2S and PH_3 but there is a overlapping of pure orbitals in them.

he minimum number of atoms in any species (moleculus or ons) indicate the central element and number of other lements indicate number of bonds formed with the central lement.

ne Typical Questions With Answers

olten NaCl conducts electricity but anhydrous HCl does xplain.

Molten $NaCl$ consists of mobile Na^+ and Cl^{-1} but anhydrous s not contain ions. Hence molten $NaCl$ is a good conf electricity but liquid anhydrous HCl is not.

re liquid HCl is a bad conductor of electricity while HCl is a good conductor of electricity. Explain. [IIT 1985]

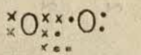
Liquid HCl is a typical covalent compound and so it like a typical non-electrolyte in pure liquid state.

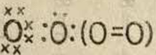
is also a polar compound and so it dissolves in the polar H_2O to produce ions conducting solution H_3O^+. This is the hydration energy is much larger than the bond energy.

H_3 is soluble in water but PH_3 is not. Explain.

NH_3 contains hydrogen bond and it is polar covalent due to e in electronegativity of atoms. But PH_3 does not contain n bond and it is pure covalent. Hence NH_3 is soluble in t PH_3 is insoluble in water.

xplain why O_2 is paramagnetic molecule (or Oxygen *does octet rule*).

The electronic structure  $(O=O)$ cannot be for O_2 molecule since it has no unpaired electrons netic).

best valence bond structure is  shown in

This has one two-electron bond, and two three-electron each containing one pair of electrons and unpaired electron. three-electron bond has the same bond strength as a onen bond or held that of a two-electron bond, this representaplains the bond order as well as paramagnetism.

5. *Water (H_2O) is a liquid but H_2S is a gas. Explain.*

Ans. Water contains hydrogen bond and forms associated $(H_2O)_n$ molecule. Therefore its boiling point becomes high. Hence it is a liquid.

H_2S is less polar and does not give any hydrogen bond. It is therefore, not associated and exists as a gas.

6. *A, B, C and D are four elements having atomic numbers* 6, 9, 10 *and* 11. *What molecules would be expected to form between*

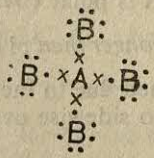
(i) *A and B* (ii) *C and C* (iii) *B and B*
(iv) *D and D* (v) *B and D*?

Mention the type of linkage.

Ans. The electronic configuration of *A*, *B*, *C* and *D* are :

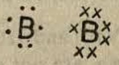
Elements	*Electronic configuration*
A–6	2, 4
B–9	2, 7
C–10	2, 8
D–11	2, 8, 1

(i) Between *A* and *B* a covalent molecule AB_4 will be formed.



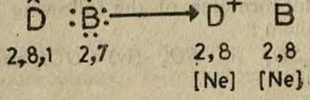
(ii) *C* is inert. No compound will be formed.

(iii) *B* has seven electrons in the outermost orbit.
Hence covalent molecule B_2 will be formed.



(iv) No molecule will be formed.

(v) *D* is electropositive and *B* is electronegative. An electrovalent molecule *BD* will be formed.



7. *When HCl gas is passed into saturated solution of sodium chloride then white crystal of NaCl is obtained. Explain.*

Ans. A precipitate is obtained when ionic product exceeds the solubility product. Since $NaCl$ solution is saturated, hence $[Na^+][Cl^-] = Ksp$, $[NaCl]$. Now HCl is passed into the solution, then Cl^- ion is increased, hence $[Na^+][Cl^-]$ now exceeds the value of Ksp, $[NaCl]$. Therefore, white crystal of $NaCl$ is obtained.

8. *Electrovalent bond is a non-directional bonding but covalent bond is a directional bonding. Explain.*

Ans. Electrovalent bond is formed due to complete transfer of electron from most electropositive to most electronegative element. Bonding is due to electrostatic forces.

But covalent bond is formed due to overlapping of orbitals in which proper direction is must, without that overlapping of orbitals will not take place.

9. *CO_2 and CH_4 are non-polar covalent compound but $CHCl_3$ is a polar covalent compound. Explain.*

Ans. Polarity and non-polarity in a bond depends upon the structure of the molecule or compound. Due to linear structure, CO_2 is non-polar covalent. Since CH_4 has symmetrical structure and resultant dipole moment is zero, hence it is non-polar covalent.

But $CHCl_3$ has unsymmetrical structure and resultant dipole moment is not zero, hence it is polar covalent.

10. *Sigma (σ) bond is stronger than pi (π) bond. Explain.*

Ans. Sigma bond is formed due to face to face overlap of orbitals but pi-bond is formed due to sidewise overlap of orbitals, hence pi-bond is weaker bond.

Exercises

Long Type

1. What are the characteristics of ionic, covalent and co-ordinate bond ? (P. U. 1922 S; P. U. 1980 A)
What types of bond exists in $NaCl$ and HCl ?
Explain why the bonds in them are not alike. (P. U. 1980 A)

2. Indicate the types of bonds present in
HCl, MgO, SO_2 and NH_4Cl. (P. U. 1982 S)
Write Lewis dot formulae for each of the following :
(i) O_2^{2-} (ii) CO_3^{2-} (iii) CN^- (iv) NCS^-. (IIT 1983)

3. Give the electron dot formulae of the following compounds and explain the nature of bonding in them :
(i) NH_4Cl (ii) H_2SO_4 (iii) SO_2 (iv) $COCl_2$ and (v) C_2H_4. (BIEC 1984)

4. (a) Write electron dot structure of HCN, NO_2^{-1}, CO_2, NO_3^{-1}.
   (b) Compare polar and non-polar covalent bonds. **(ISM 1985)**

5. (a) Atoms A, B and C occur in the same period and have one, six and seven valence electrons respectively.
   (i) Will the bond between B and C be predominently ionic or covalent ? Explain.
   (ii) Write the electronic structure of the compound formed between B and C.
   (iii) Will the bond between A and B be predominently ionic or covalent ? Explain.
   (iv) Write the electronic structure of the compound formed between A and B. **(Roorkee 1984)**
   Write an essay on electronic theory of valency. **(BIT Messra 1982)**

6. Write the electron dot structures of
   (i) HNO_3 (ii) $Na_2S_2O_2$ and (iii) O_2. **(ISM 1984)**

6. (i) Define the following :
   (a) Bond order (b) Bonding molecular orbital (c) Antibonding molecular orbital.
   (ii) Calculate the bond order of N_2^+ and O_2 molecule. **(DSB 1982)**
   (iii) Calculate the bond order of He_2^+, N_2 molecule, He_2 molecule and O_2^+ ion. **(AISB 1981)**

7. (a) Why the idea of electronic theory was introduced ?
   (b) What is the basis of electronic theory of valency ?
   (c) Define and explain electrovalency with the help of $MgCl_2$.

8. (a) Discuss the relationship of electronegativity with the type of chemical bond formed.
   (b) In general what conditions cause two atoms to combine to form each of the following :
   (i) a bond that is covalent (ii) a bond that is ionic.
   (Delhi State SSC 1978)

9. (a) Which type of bonding is likely in a binary compound when both elements are
   (i) non-metals and (ii) ion-forming with opposite electric charges ?
   (b) Explain why ordinarily H_2S is a gas and H_2O is a liquid even though S and O are the elements of the same group in the periodic table and S has a higher atomic weight.
   (c) Which of the following hydrogen halides has the most polar molecule and why ?
   HI, HBr, HCl, HF ? (All India Board SSC 1978)

10. What do you mean by covalency ? Distinguish between electrovalency and covalency.
(R. U. 1968; B. U. '81; Roorkee '83; B.I.T. Messra '83; WBJEE '83)

11. Write down the Lewis dot formulae of the following :
A. (a) SO_4^{2-} (b) H_3PO_4 (c) BF_3 (d) NF_2. **(Roorkee 1983)**
B. (a) HCl (b) NH_4Cl (c) SO_4^{-2} (d) NO (e) PCl_5.

12. Write notes on : (i) σ-bond (ii) π-bond (iii) hydrogen bond.

Short Type

13. Covalent compounds have as a rule low boiling and melting points as compared to electrovalent compounds. Give reasons.

14. Assign electronic formula of the following :

(i) Magnesium chloride (ii) Sulphur dioxide (iii) water (iv) Hydronium ions (v) Sodium carbonate (vi) Phosphours pentachloride (vii) Boron trifloride.

15. Write down the electron dot formula of the following :

(i) $KMnO_4$ (ii) $K_2Cr_2O_7$ (iii) Nitric acid (iv) Carbon tetrachloride (v) Sodium sulphide (vi) Ammonium chloride.

16. Show by dot formula that NH_4Cl and H_2SO_4 contain all the types of bond.

17. Explain why sodium chloride has high melting point compared to ethyl chloride ? (I.S.C. 1980)

[**Hint** : $NaCl$—electrovalent, C_2H_5Cl—covalent]

18. State three properties in which electrovalent and covalent compounds differ from one another.

19. (a) How many sigma-bonds and how many pi-bonds are present in a benzene molecule ?

(b) Write down the resonance structures of nitrous oxide. **(IIT 1985)**

20. On the basis of the electronic theory of valency explain why do the atoms combine together.

21. With the help of one example explain what is meant by a polar covalent bond.

22. Give the valency of :

(i) Sulphur in Na_2SO_4 (ii) Chlorine in $KClO_4$
(iii) Chromium in $K_2Cr_2O_7$ (iv) Iodine in ICl_3.

(Roorkee 1977)

23. What do you mean by hybridisation ?

What type of hybridisation is found in :

(i) CO_2 (ii) NH_3 (iii) C_2H_2 (iv) H_2O (v) SO_4^{-2} ?

24. **Explain the following :**

(a) O_2 is paramagnetic (b) H_2O is a liquid but H_2S is a gas (c) HCl (acid) conducts electricity but CCl_4 does not conduct electricity (d) KCl is more polar than $NaCl$ (e) KCl gives precipitate with silver nitrate solution but pure chloroform does not give precipitate with $AgNO_3$ solution.

25. **Name :**

(a) Two isoelectronic species (b) two isosters (c) two compounds in which octate rule failed (d) one element in which octet rule failed (e) two electron defficient compounds (f) two compounds in which there are three types of bond (g) three compounds in which there is covalent co-ordinate bond (h) two compounds in which there is one electron bonding (i) two compounds in which there is three electron bonds.

26. Define dipole moment. How can you estimate polarity % of ionic character and shape of the molecule ?

27. Explain the following :

(a) CO_2 has no dipole moment, but SO_2 does,
(b) CH_4 has no dipole moment, but CH_2Cl_2 does,
(c) BF_3 has no dipole moment, but NF_3 does,
(d) NH_3 is dipole moment of NH_3 is considerably higher (=1·47 D) than the dipole moment of NF_3 (0·2 D).

28. What is the valency of Mn in the following compounds ?
(i) MnO_2 (ii) $MnSO_4$ (iii) K_2MnO_4 (iv) K_3MnF_6. **(IIT 1978)**

29. Classify the following compounds as ionic or covalent :
(i) MgF_2 (ii) $BrCl$ (iii) CBr_4 (iv) C_2H_2 (v) CuS (vl) PH_3.
(IIT 1978)

30. Give the electronic formula of
(i) Water (ii) Acetylene (iii) Ammonium bromide. **(Roorkee 1979)**

31. Give the structural formula for the following :
(i) Phosphorus acid H_3PO_3 (ii) Pyrophosphoric acid $H_4P_2O_7$.
(IIT 1981)

32. Indicate the nature of bond, ionic or covalent, in the following substances :
(i) CH_4 (ii) Cl_2 (iii) NH_3 (iv) K_2O (v) CH_3OH (vi) CaH_2.
(IIT 1966)

33. Indicate the nature of bonding in the following :
(i) NH_3 (ii) CO_2 (iii) H_2O (iv) CaO (v) LiH (vi) $AlCl_3$ (vii) CH_4 (viii) N_2 (ix) CaC_2 (x) Al_2O_3 (xi) NH_4^+ (xii) $NaCl$ (xiii) H_2S (xiv) C_2H_2.
(IIT 1970)

34. Indicate the uature of bonding in the following :
(i) K_2O (ii) Cl_2O (iii) CCl_4 (iv) Mg_3N_2 (v) NaI (vi) C_2H_4.
(IIT 1971)

35. Indicate the nature of bonding in the following :
(a) Diamond (b) NaH (c) Silica (SiO_2) (d) $SnCl_4$ (e) ClO_4^- (f) $MgCl_2$.
(IIT 1975)

36. Fill up the blank—
(i) The total no. of electrons between two nitrogen atoms in N_2 are——— (ii) $NaCl$ is———but CCl_4 is———polar. (iii) SO_3 contains———and ———bonds. (iv) NH_4Cl contains—— ———and———bonds. (v) HCl (g) is———polar but HCl (acid) is———. (vi) $AlCl_3$ is an———defficient compound. (viii) CO_2 has got———hybridisation. (ix) The total number of σ and π-bonds in C_2H_4 is——and ———respectively. (x) H_2O is a liquid because it contains———bond. (xi) NH_3 has got———bond angle than CH_4.

37. **Match Type :**

MATCH A WITH B.

A	*B (shape)*
(1) NH_3	(a) Triangular
(2) CH_4	(b) V-shaped
(3) H_2O	(c) Pyramidal
(4) C_2H_4	(d) Linear
(5) C_2H_2	(e) Teterahedral

38. Match *A* and *B* in the following :

A	*B*
(i) Covalent bond	(vii) HCl
(ii) Ionic bond	(viii) NH_4^+
(iii) Single covalent bond	(ix) H_2O
(vi) Co-ordinate bond	(x) $CaCl_2$
(v) Multicovalent bond	(xi) C_2H_2
(vi) Polar covalent bond	(xii) CH_4

39. State whether the following statements are true or false :

(i) Ionic compounds conduct electricity in the molten state.
(ii) Melting point of $NaCl$ is much higher than that of $AlCl_3$.
(iii) A polar bond is formed between two atoms which have similar electronegativities.
(iv) When two atoms approach to form a bond between them, the potential energy decreases.
(v) Covalent bonds are directional whereas ionic bonds are non-directional. **(IIT 1980)**

Select and Write Correct answer for the following :

40. The formula of a metal phosphate is $MHPO_4$. The formula of a metal chlorate will be :

(1) $MClO_3$ (2) $M(ClO_3)_2$ (3) M_2ClO_3 (4) $M_2(ClO_3)_3$ (5) None.

41. In covalency :

(1) the transference of electrons takes place
(2) sharing of electrons takes place
(3) the electrons are shared by only one atom
(4) none of these takes place. **(PMDT 1976, '78, '81)**

42. In double bond connecting two atoms there is sharing of :

(1) 2 electrons (2) 4 electrons (3) electron (4) all electrons. **(CPMPT 1981)**

43. $NaCl$ crystal is made up of

(1) $NaCl$ molecules (2) Na^+ and Cl^- ions
(3) Na and Cl atoms (4) none of these. **(NCERT 1976)**

44. The enhanced force of cohesion in metals is due to :

(1) the covalent linkage betwven atoms
(2) the electrovalent linkage between atoms
(3) the lack of exchange of valency electrons
(4) the exchange energy of mobile electrons. **(NCERT 1972)**

45. When sodium and chlorine react, energy is

(1) released, and ionic bonds are formed
(2) released, and covalent bonds are formed
(3) absorbed, and ionic bonds are formed
(4) absorbed, and covalent bonds are formed. **(NCERT 1973)**

46. The nitrogen atom has 7 protons and 7 electrons. The nitride will have

(1) 7 protons and 10 electrons (2) 4 protons and 7 electrons
(3) 4 protons and 10 electrons (4) 10 protons and 7 electrons. **(NCERT 1977)**

47. Which of the following element has got multiple covalent bond ?
(1) C_2H_4 (2) CO_2 (3) C_2H_2 (4) N_2 (5) all the above.

48. Which among the following elements has the tendency to form covalent compounds ?
(1) Berylium (2) Barium (3) Magnesium (4) Calcium.
(NCERT 1978)

49. Noble gases do not react with other elements because—
(1) they are monoatomic
(2) they are not found in abundance
(3) the size of the atoms are very small
(4) they have completely paired up and stable electron shell.
(CPMT 1981)

50. An electrovalent compound is made up of :
(1) electrically charged atom (2) neutral molecule (3) neutral atoms
(4) electrically charged atoms or group of atoms. **(CPMT 1981)**

51. The molecule having one unpaired electron is—
(1) NO (2) CO (3) CN^- (4) O_3. **(IIT 1985)**

52. The valence shell of calcium contains :
(1) 2 electrons (2) 4 electrons
(3) 6 electrons (4) 8 electrons. **(MNREC 1982)**

53. Which of the following is covalent ?
(1) H_2 (2) MgO (3) $NaCl$ (4) Na_2S. **(IIT 1980; MNR '82)**

54. The number of valence electrons in carbon atom (at. no.=6) is :
(1) 0 (2) 2 (3) 4 (4) 6. **(MNREC 1982)**

55. Among the following the molecule that is linear is :
(1) CO_2 (2) SO_2 (3) NO_2 (4) ClO_2. **(IIT 1982)**

56. The ion that is iso-electronic with CO is :
(1) CN^{-1} (2) O_2^+ (3) O_2^{-1} (4) N_2^+. **(IIT 1982)**

57. The number of neutrons in positive Zn^{2+} ion with mass no. 70 is :
(1) 34 (2) 36 (3) 38 (4) 40. **(IIT 1979)**

58. Molten $NaCl$ conduct electricity due to pressure of
(1) free electrons (2) free ions
(3) free molecules (4) atoms of Na and Cl. **(IIT 1981)**

59. The bond order of individual carbon-carbon bonds in benzene is :
(1) one (2) two (3) between one and two
(4) one and two alternately. **(IIT 1981)**

60. The angle between two covalent bonds is maximum in—
(CH_4, H_2O, CO_2). **(IIT 1981)**

61. Which of the following compounds are covalent ?
H_2, CaO, KCl, Na_2S. **(IIT 1981)**

62. Pair of molecules which form strongest inter-molecular hydrogen bond is :
SiH_4 and SiF_4, CH_3COCH_3 and $CHCl_3$,
$HCOOH$ and CH_3COOH. **(IIT 1981)**

63. Element X is strongly electropositive and element Y is strongly electronegative. Both are univariant. The compound formed would be
X^+Y^-; X^-, Y^-; $X-Y$; $X \rightarrow Y$. **(IIT 1980)**

64. Molecule in which the distance between the two adjacent carbon atoms is largest is :
(1) ethane (2) ethene (3) ethyne (4) benzene. **(IIT 1981)**

65. Pick out the molecule which has zero dipole moment :
(1) CH_2Cl_2 (2) H_2O (3) BCl_3 (4) CO.

66. Which of the molecule have a dipole moment ? :
(1) CCl_4 (2) CO_2 (3) C_6H_6 (4) HCl.

67. CO_2 has zero dipole moment because
(1) carbon and oxygen have same moment
(2) carbon and oxygen have zero electronegativity
(3) its structure is linear
(4) carbon and oxygen atom are arranged in the form of a bent chain in it.

68. When a neutral atom is converted into a cation its :
(1) At.Wt. increases (2) At.Wt. decreases
(3) size increases (4) size decreases. (NCERT 1982)

69. A bond with maximum covalent character between non-metallic element is found
(1) between identical atoms
(2) between chemically similar atoms
(3) between atoms of widely differing electronegativity
(4) between atoms of the same size. (NCERT 1982)

70. The Bond order for N_2 molecule is
(a) 2 (b) 4 (c) 5 (d) 3.

71. On hybridisation of one *s* and one *p* orbitals we get :
(1) two mutually perpendicular orbitals
(2) two orbitals at 180
(3) four orbitals directed tetrahedrally
(4) three orbitals in a plane. (IIT 1984)

CHAPTER 5

HYDROGEN, HEAVY HYDROGEN, AND HEAVY WATER

Symbol—H Electronic configuration—$1S^1$

5.1. Introduction

It was discovered by Henry Cavendish in 1776. Hydrogen is the first member of the periodic table. It is the lightest element. Its atomic weight is 1·008. Its electronic configuration is $1s^1$.

5.2. Position of Hydrogen in the Periodic Table

The position of hydrogen in the periodic table is anomalous. Hydrogen resembles both the alkali metals and halogens. This dual behaviour of hydrogen can be explained with the help of its peculiar electronic arrangement.

5.3. Similarity with Alkali Metals

(i) **Electronic structure** : Both have one electron in their outermost orbit.

$H_1 = 1$ $Na_{11} = 2, 8, 1.$

(ii) **Electropositive character** : Both are electropositive in character being capable of losing one electron to form H^+, Na^+, K^+ ion etc.

(iii) **Affinity for non-metals** : Both have strong affinity for non-metals but little for metals. It combines with halogens to form halides (HCl, $NaCl$).

(iv) **Evolution at cathode** : Both hydrogen and alkali metals are liberated at the cathode.

5.4. Similarity with Halogens

(i) **Electronic configuration** : Both contain one electron less than the maximum number in their outermost orbit.

$H = 1$ $Cl_{17} = 2, 8, 7$
(one electron short) (one electron short)
$He_2 = 2$ $Ar_{18} = 2, 8, 8$

(ii) **Non-metallic character** : Both Hydrogen and Halogens are typical non-metals.

(iii) **Formation of negative ion** : Both can take up one electron to form hydrides and chlorides. Both on electrolysis evolve H_2 and Cl_2 on anode.
Fused NaH gives H_2 at anode and fused $NaCl$ gives chlorine at anode.

(iv) **Ionisation potential** : Both hydrogen and halogens possess same ionisation potential.

$$H = 13{\cdot}54 \text{ eV} \qquad Cl = 13{\cdot}0 \text{ eV}$$

(v) **Atomicity** : Both hydrogen and halogens form diatomic molecules with covalent bonds.

$$H—H \qquad Cl—Cl$$

The Alkali metals however, have mono-atomic molecules. Alkali metals form monovalent molecules.

(vi) **Formation of similar type of compounds** : Both form similar types of compounds with carbon, silicon and germanium.

$$CH_4, SiH_4 \text{ and } GeH_4 \qquad CCl_4, SiCl_4 \text{ and } GeCl_4$$

(vii) **Replacement of hydrogen by halogens** : Hydrogen can be replaced by halogens in hydrocarbons, alkyl radicals etc. This shows the similar nature of hydrogen with halogens.

$$C_2H_6 \xrightarrow{Cl_2} C_2H_5Cl \xrightarrow{Cl_2} C_2H_4Cl_2 \xrightarrow[\text{excess}]{Cl_2} C_2Cl_6$$

It is evident from the above discussion that hydrogen shows dual character. It can gain an electron like halogens and lose an electron like alkali metals.

However, in some respects it differs from both e.g. its oxide, H_2O, is neither basic like the oxides of alkali metals, nor acidic like the oxides of halogens. It is neutral.

Na_2O	H_2O	Cl_2O_7
Basic	Neutral	Acidic

Thus **Thomson** suggested the position of hydrogen in the periodic table as anomalous. It should be allotted a separate and distinct place unassociated with any particular group as the first element of the periodic table.

5.5. Preparation

The chief sources from which hydrogen is prepared are water, acids and alkalies. Various methods are given below :

(a) **From Water** : Hydrogen can be prepared from water by the following methods :

(i) **Cold Water** : Active metals, such as sodiunm, potassium and calcium decompose water at the room temperature with the evolution of hydrogen :

$$2Na + 2H_2O \rightarrow 2NaOH + H_2 \uparrow$$
$$2K + 2H_2O \rightarrow 2KOH + H_2 \uparrow$$
$$Ca + 2H_2O \rightarrow \underset{\text{cal. hydroxide}}{Ca(OH)_2} + H_2 \uparrow$$

In the case of sodium and potassium the reaction is quite vigorous. If in place of sodium its amalgam is employed, the reaction is less vigorous and be easily controlled.

(ii) **Hot water** : Metals, such as zinc powder, magnesium powder and aluminium powder, decompose boiling water to form metal oxides and hydrogen.

$$Mg + H_2O \rightarrow MgO + H_2 \uparrow$$

$$Al + 3H_2O \rightarrow \underset{\text{Aluminium oxide}}{Al_2O_3} + 3H_2 \uparrow$$

(iii) **Steam** : Metals, such as iron, cobalt, nickel and tin, decompose steam to form hydrogen. In the case of iron, the reaction is reversible.

$$3Fe + 4H_2O \rightleftharpoons \underset{\text{Ferrosoferric oxide}}{Fe_3O_4} + 4H_2 \uparrow$$

(iv) **Metal Hydrides** : Metal hydrides decompose water at room temperature to form metal hydroxides and hydrogen. Reactions with sodium hydride and calcium hydride (hydrolith) are given below :

$$2NaH + 2H_2O \rightarrow 2NaOH + 2H_2 \uparrow$$

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2 \uparrow$$

(b) **From Acids** : A number of metals, such as zinc, magnesium and iron react with dilute hydrochloric acid and dilute sulphuric acid at room temperature with the evolution of hydrogen.

$$Zn + H_2SO_4 \rightarrow \underset{\text{zinc sulphate}}{ZnSO_4} + H_2$$

$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$$

Many metals like copper, mercury, silver and gold do not decompose dilute sulphuric acid or dilute hydrochloric acid.

(Refer to Electrochemical series)

(c) **From Alkalies** : Zinc, aluminium, tin and powdered silicon react with hot solution of alkalies to produce hydrogen.

$$Zn + 2NaOH \rightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2} + H_2 \uparrow$$

$$2Al + 2NaOH + 2H_2O \rightarrow \underset{\text{Sod. aluminate}}{2NaAlO_2} + 3H_2 \uparrow$$

$$Sn + 2NaOH + H_2O \rightarrow \underset{\text{Sod. stannate}}{Na_2SnO_3} + 2H_2 \uparrow$$

$$Si + 2NaOH + H_2O \rightarrow \underset{\text{Sod. silicate}}{Na_2SiO_3} + 2H_2 \uparrow$$

(d) **From Nitric acid** : Dilute nitiric acid reacts with magnesium and managanese to give hydrogen.

$$Mg + 2HNO_3 \rightarrow Mg(NO_3)_2 + H_2 \uparrow$$

5.6. Industrial Preparation of Hydrogen (Manufacture of Hydrogen)

The chief industrial methods for the preparation of hydrogen are given below :

(i) **Lane's process** : When superheated steam is passed over heated iron in a suitable furnace hydrogen is produced according to the equation given below :

$$3Fe+4H_2O \rightleftharpoons Fe_3O_4+4H_2+35{\cdot}6 \text{ cal.}$$

This is a reversible reaction.

(ii) **Bosch process** : When steam is passed over red hot coke (1000°C) then water gas is obtained.

$$C+H_2O \rightarrow CO+H_2$$

It is difficult to separate CO from H_2. Hence this mixture is mixed with steam at 500°C in presence of Fe_2O_3 (catalyst) and Cr_2O_3 (promoter) then CO_2 and H_2 are obtained.

$$CO+H_2O \rightarrow CO_2+H_2$$

CO_2 is removed by dissolving it in water under pressure. The traces of CO are removed by passing it through ammonical Cu_2Cl_2 solution.

(iii) **Electrolysis of water** : This method can be used for the manufacture of hydrogen, wherever electric power is cheap. Water is made a conductor of electricity by the addition of sulphuric acid or sodium hydroxide. Hydrogen is evolved at the cathode and is collected. Oxygen produced at the anode is collected as a by-product. The reaction takes place at the electrodes as described below :

At the cathode :

$$H^+ + e^- \rightarrow H;\ H+H \rightarrow H_2 \uparrow$$

At the anode :

$$2OH^- \rightarrow H_2O+O+2e^-;\ O+O \rightarrow O_2 \uparrow$$

(iv) **From Natural Gas** : Methane (CH_4) is the major constituent of natural gas obtained from petroleum fields. Natural gas is mixed with steam and the mixture is passed over a nickel catalyst at about 900°C. A mixture of carbon monoxide and hydrogen is obtained and is separated as described in the first method.

$$CH_4+H_2O \xrightarrow{Ni-Cr} CO+3H_2$$

$$CH_4 \xrightarrow[1000^\circ C]{\text{Cracking}} C+2H_2$$

(v) **From Hydrolith** : When hydrolith (CaH_2) reacts with water (cold) then hydrogen is obtained.

$$\underset{\text{Calcium hydride}}{CaH_2} + 2H_2O \rightarrow Ca(OH)_2+3H_2$$

5.7. Physical properties

(i) Hydrogen is a colourless, odourless and tasteless gas. (ii) It can be liquefied by cooling under pressure (on rapid evaporation liquid hydrogen solidifies to give a snow-white solid).

Its boiling point and melting point are −253°C and −259°C respectively. (iii) It is sparaingly soluble in water (iv) It is the lightest gas known. It has, therefore, the fastest rate of diffusion. (v) Hydrogen has three isotopes—hydrogen (also called protium), deuterium (heavy hydrogen) and tritium having atomic masses 1, 2 and 3 respectively. Ordinary hydrogen contains about 0·016 per cent of deuterium and a very minute quantity of tritium.

5.8. Chemical properties

(a) Hydrogen is neutral to litmus.

(b) **Combustibility** : It is a combustible gas and burns in oxygen or air with a pale blue flame to produce water. It is a non-supporter of combustion. A mixture of hydrogen and oxygen in right proportion explodes violently when a flame is brought near it.

$$2H_2+O_2 \rightarrow 2H_2O.$$

(c) **Reaction with Non-metals** : Hydrogen combines with a number of non-metals under suitable condition.

(i) The reactivity with halogens decreases from F_2 to I_2.

$$H_2+X_2 \rightarrow 2HX \ (X=F, Cl, Br, I)$$

(ii) The reactions with other non-metals take place as follows :

$$H_2+S \rightarrow H_2S$$

$$N_2+3H_2 \rightarrow 2NH_3$$

(d) **Reaction with Metals** : Hydrogen reacts with strongly electropositive metals, such as sodium, potassium and calcium on heating to form metal hydrides.

$$2Na+H_2 \rightarrow 2NaH$$

$$Ca+H_2 \rightarrow CaH_2$$

(e) **As Reducing agent** : It is a strong reducing agent. It reduces metallic oxides to corresponding metals.

$$\underset{\text{Copper oxide}}{CuO}+H_2 \rightarrow Cu+H_2O$$

$$\underset{\text{Silver oxide}}{Ag_2O}+H_2 \rightarrow 2Ag+H_2O$$

$$2AgCl+H_2 \rightarrow 2Ag+2HCl$$

(f) **Hydrogenation** : When hydrogen is passed through vegetable oils like ground nut oil in the presence of finely divided nickel (catalyst) these are converted into solid fats. This process is known as *hydrogenation of oils* and is employed in the manufacture of vanaspati ghee. During this process the liquid, unsaturated organic compounds present in the oil are converted into the corresponding solid saturated compounds.

Types of Hydrogen

5.9. Nascent Hydrogen

The hydrogen obtained during the chemical reaction in the beginning is known as **Nascent hydrogen.** In this state it contains high energy because it is envolved of high pressure. Hence it is very reactive.

This state of hydrogen is called atomic state. It is easily converted into molecular state and its reactivity is decreased. The nascent hydrogen is more reactive than molecular hydrogen.

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + \underset{\text{(Nascent)}}{2\text{'}H\text{'}}$$

$$2\text{'}H\text{'} \rightarrow H_2 \text{ (Molecular } H_2\text{)}$$

Ex. (i) Acidified potassium permanganate solution remains unaffected by hydrogen gas. But when zinc is placed in the solution of acidified $KMnO_4$ then it is converted to colourless manganous salt and potassium chlorate to chloride.

$$Zn + 2HCl \rightarrow ZnCl_2 + 2\text{'}H\text{'}$$

(a) $\underset{\text{Violet}}{2KMnO_4} + 3H_2SO_4 + 10\text{'}H\text{'} \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O$

(b) $KClO_3 + 6\text{'}H\text{'} \rightarrow KCl + 3H_2O$

Ex. (ii) When hydrogen is passed through acidified $FeCl_3$ solution it remains unaffected. But if Zinc is placed in the solution, the reduction of ferric chloride into ferrous chloride takes place immediately.

$$Zn + 2HCl \rightarrow ZnCl_2 + 2H$$
$$FeCl_3 + H \rightarrow FeCl_2 + HCl$$
$$Fe^{+++} + H \rightarrow Fe^{++} + H^+$$

Important sources of Nascent hydrogen are :

(i) a mixture of zinc and dilute H_2SO_4. (ii) a mixture of Sn and HCl or Fe and H_2O in presence of a small quantity of HCl, (iii) Na and absolute alcohol and Zn-Cu couple and alcohol, (iv) electrolysis of acidulated water.

Theories of Nascent hydrogen :

(i) **Atomic hypothesis** : Formerly it was thought that in the case of ordinary hydrogen during reduction energy has to be supplied for breaking the molecules into atoms while the nascent hydrogen being atomic attacks directly.

This theory, however, fails to explain why nascent hydrogen from different sources is not equally effective. Thus nascent hydrogen from Zn and dil. H_2SO_4 will readily reduce chlorates into chlorides but that from Na-amalgam and water has no effect.

(ii) **Energy hypothesis :** Another explanation for the increased activity of nascent hydrogen is that **part of energy** liberated as a result of reaction producing hydrogen becomes associated with the hydrogen evolved so that nascent hydrogen is simple hydrogen molecules possessing extra energy. Since the energy liberated in different reactions is different, the reactivity of nascent hydrogen produced will also be different. For example Zn dissolves by H_2SO_4 by electron transfer and evolution of hydrogen takes place with the removal of electron by H^+ ion simultaneously.

$$Zn \rightarrow Zn^{++} + 2e^{-1}$$
$$H^+ + e^{-1} \rightarrow H$$

(ii) **Internal Pressure Theory :** According to this theory hydrogen at the moment of its formation is in the form of very small bubbles with very high internal pressure, thus this high internal pressure is the cause of great activity of nascent hydrogen.

5.10. Atomic Hydrogen

Preparation : (i) Langmuir (1916) Electric Arc Method. : When ordinary hydrogen is passed through an electric arc maintained between tungsten electrodes then hydrogen molecules are dissosciated to hydrogen atoms as fig. 5.1.

$$H_2 \rightleftharpoons 2H$$

This led to the discovery of atomic hydrogen welding torch.

(ii) **Photochemical method :** Cairo and Frink (1922) prepared atomic hydrogen by exposing hydrogen mixed with mercury vapour to the resonance radiation of mercury arc.

(iii) **Bonhoeffer's method :** When ordinary hydrogen is passed at low pressure through high tension discharge tube then atomic hydrogen is obtained.

$$H_2 \rightleftharpoons 2H - x \text{ cals.}$$

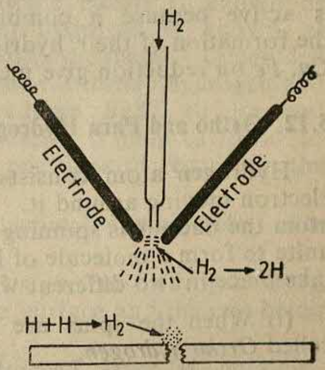


Fig. 5.1

Properties :

(i) It is unstable (life period $\times \frac{1}{2}$ of second) and is thus extremely reactive. The half life increases at low pressure in the absence of catalyst since a million collisions must take place.

(ii) It combines with another hydrogen atom to form' a molecule and evolving large amount of heat.

$$H + H \rightleftharpoons H_2 + 102{\cdot}8 \text{ cals.}$$

This is made use in an *atomic hydrogen blow pipe*.

(iii) It combines with non-metals and metals to form hydrides. Thus it reacts with sulphur, phosphorus, arsenic to form H_2S, PH_3 and AsH_3 and with Na, K, Li to form hydrides.

$$S+2H \rightarrow H_2S$$
$$Na+H \rightarrow NaH$$

(iv) It combines with O_2 to form H_2O and with CO to form formaldehyde.

$$2H+O_2 \rightarrow H_2O_2$$
$$CO+2H \rightarrow H.CHO$$

(v) It reduces oxides, chlorides of certain metals like Cu, Ag, Hg into metal and ethylene into ethane.

$$CuO+2H \rightarrow Cu+H_2O$$
$$Ag_2O+2H \rightarrow 2Ag+H_2O$$
$$C_2H_4+2H \rightarrow C_2H_6$$

5.11. Active Hydrogen

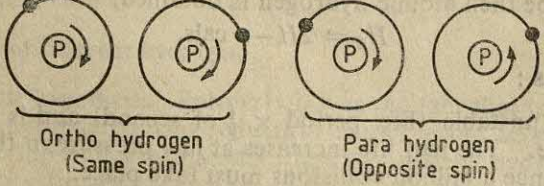
It is prepared by passing stream of hydrogen at 0·5 mm in presence of silent electric discharge at 30000 volts. This hydrogen is active because it combines directly with P, As, Pb, S etc. with the formation of their hydrides. At ordinary temperature oxides of Cu, Fe on reduction give metals.

5.12. Ortho and Para Hydrogen

Hydrogen atom consists of nucleus with one proton and an electron moving around it. It has been established that in hydrogen atom the nucleus is spinning like a top. Two such hydrogen atoms unite to form a molecule of hydrogen and in that case the union can take place in two different ways :

(i) When the spins are in the same direction, the molecule is called *Ortho hydrogen.*

(ii) When the spins are in opposite direction, it is known as *Para-hydrogen.*



At room temperature ordinary hydrogen is an equilibrium mixture of 75% ortho and 25% para forms but if the temperature is lowered the proportion of ortho form decreases while that of para form increases, till at −253°C practically pure para form is obtained.

Bonhoffer and Harteck in 1929 were able to prepare para hydrogen by absorbing ordinary hydrogen on activated charcoal at 253°C. It is, however, not possible to obtain ortho form in a pure state.

The two forms differ slightly in their physical properties while they are similar in their chemical properties. Their specific heats and thermal conductivities are different. *Ortho form is more stable than para form* and para hydrogen always lends to refer to ortho form. Para hydrogen is converted to ortho hydrogen by treating it with atomic hydrogen.

This is not peculiar to hydrogen, but will occur in all homonuclear diatomic molecules in which the nuclei have spin.

5.13. Occuluded Hydrogen

Metals like platinum and palladium can absorb large volumes of hydrogen under special conditions. It was observed by Graham that palladium absorbs 935 times its own volume of hydrogen at red heat. Colloidal palladium absorbs up to 2050 times its own volume of hydrogen. Such absorbed hydrogen by the metals is known as *Occuluded hydrogen.* This phenomena of hydrogen is known as *occlusion.* It can be given out by heating the metal. Occuluded hydrogen is found to be more reactive than ordinary hydrogen and it is very strong reducing agent. It reduces $HgCl_2$ to Hg and combines with chlorine and iodine in the dark. It reduces ferric to ferrous salts. Different views have been put forward regarding the nature of occluded hydrogen.

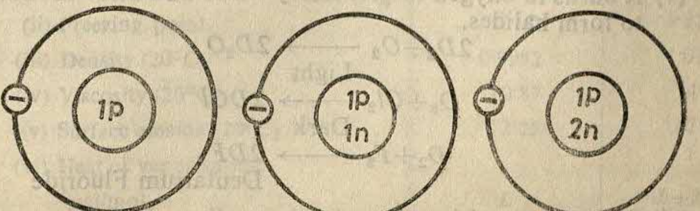
(i) It was formerly believed that chemical combination takes place between the metal and hydrogen.

(ii) **Holt and Firth** (**1913**) believed that a part of hydrogen is in the form of a condensed layer on the surface and the rest being absorbed in the interior of the metal.

(iii) According to Langmuir the adsorbed layer is unimolecular in thickness.

5.14. Isotopes of Hydrogen

Hydrogen has got three isotopes each with one electron and one proton, with one and two neutrons respectively.



Hydrogen Deuterium Tritium

Test for Hydrogen : It burns with blue flame and it is adsorbed by heated palladium (*Pd*).

Uses of Hydrogen : (i) As a rocket fuel, (ii) in aeroplane lifting, (iii) in the manufacture of vegetable ghee (Dalda etc.), (iv) in oxy-hydrogen flame in welding.

5.15. Preparation of Deuterium or Heavy hydrogen

(i) From liquid hydrogen : This method is, however, of historical interest only.

From Heavy Water :

(i) **By electrolysis of heavy water** : 6000 parts of ordinary water contains 1 part of heavy water. When ordinary water containing alkali is electrolysed at 0-30°C between *Ni*-electrodes and current of 250 amperes, it is possible to get 1 c.c of heavy water from 20 litres of ordinary water. When heavy water is electrolysed, fairly pure heavy hydrogen is obtained at the cathode.

$$2D_2O \rightarrow 2D_2+O_2$$

(ii) **By decomposition of heavy water by tungsten or zinc** : The vapours of heavy water are led into decomposition chamber containing electrically heated (1000°C) tungsten filament. The vapours decompose to give heavy hydrogen.

$$2D_2O \rightarrow 2D_2+O_2$$

Properties :

(i) It is colourless, tasteless, odourless gas having twice the density of ordinary hydrogen.

(ii) It's boiling point (−249·5°C), m.p. (−254·5°C), latent heat of fusion (52·3 cal/mole) and vapourisation (355·4 cal/mole) are all higher than ordinary hydrogen.

(iii) It also exists in ortho and para forms like ordinary hydrogen.

(iv) **In chemical properties** it resembles ordinary hydrogen in all respects, the only difference being in the slackness of the reactions due to the heavy nature of its molecules.

(v) It burns in oxygen to give heavy water and also in halogens to form halides.

$$2D_2+O_2 \longrightarrow 2D_2O$$

$$D_2+Cl_2 \xrightarrow{\text{Light}} 2DCl$$

$$D_2+F_2 \xrightarrow{\text{Dark}} 2DF$$

Deutarium Fluoride

(vi) It combines with sodium to give sodium deuteride.

$$2Na+D_2 \rightarrow 2NaD$$

(vii) It reacts with ethylene to give ethylene deuteride.

$$D_2 + C_2H_4 \xrightarrow[260^\circ C]{Ni} C_2H_4D_2$$

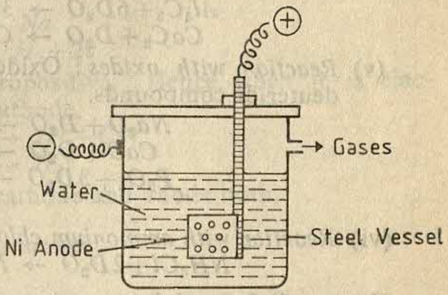
Uses :

(a) as tracers in studying the mechanism of various reactions,
(b) as a source of deuterous in transmutation of elements,
(c) in the preparation of deuterium compounds.

HEAVY WATER (D_2O) OR DEUTERIUM OXIDE

Introduction : It was discovered by H.C. Urey in 1932. It is denoted by the formula D_2O. The ordinary water contains one part of heavy water in 6000 parts of it.

Preparation : It is prepared by the method suggested by Mac Donald and Lewis in 1933. About 20 litres of ordinary water containing alkali are electrolysed. The electrolysis is carried out in steel cell (cathode) and perforated Nickel sheets act as anode. A current of 250 amperes is employed. Electrolysis is continued until the volume is reduced to 90%. One-tenth of the remaining portion is neutralised with CO_2 and the rest distilled. The two portions are mixed and the process is repeated until the volume is reduced to about 0·5 c.c. The residue is heavy water.



Heavy water can also be obtained by the fractional distillation of ordinary water.

Properties. Heavy water differs from ordinary water in the following physical properties :

Properties	H_2O	D_2O
(i) Boiling point	100°C	101·42°C
(ii) Freezing point	0°C	3·82°C
(iii) Density (20°C)	0·9982	1·017
(iv) Viscosity (20°C)	10·87	14·2
(v) Surface tension (20°C)	72·75	67·8
(vi) Heat of vaporisation cal/mol	L	$L+259$
(vii) Dielectric constant	82·0	80·5

Heavy water is injurious to living cells.

Chemical : There is little difference in chemical properties of ordinary water and heavy water. Hydrogen atoms are easily interchanged in chemical reactions with deuterium atom.

(i) *Reaction with metals* : It evolves deuterium.

$$2Na+D_2O \rightarrow \underset{\text{Sodium deutroxide}}{2NaOD} + D_2$$

(ii) *Reaction with acids* : It reacts with HCl to form deutrochloride.

$$HCl+D_2O \rightarrow DCl+HDO$$

(iii) *Reaction with metal nitride* : It gives deutero-ammonia.

$$Mg_3N_2+3D_2O \rightarrow 3MgO+2ND_3$$

(iv) *Reaction with metal carbides* : It gives deuteromethane with aluminium carbide and deutro acetylene with calcium carbide.

$$Al_4C_3+6D_2O \rightarrow 3CD_4+2Al_2O_3$$
$$CaC_2+D_2O \rightarrow C_2D_2+CaO$$

(v) *Reaction with oxides* : Oxides dissolve in heavy water form deuteride compounds.

$$Na_2O+D_2O \rightarrow 2NaOD$$
$$CaO+D_2O \rightarrow Ca(OD)_2$$
$$P_2O_5+3D_2O \rightarrow \underset{\text{Heavy phosphoric acid}}{2D_3PO_4}$$

(vi) *Reaction with ammonium chloride* : It gives ND_4Cl.

$$NH_4Cl+2D_2O \rightarrow ND_4Cl+2H_2O$$

Uses : (i) In studying reactions occurring in living organisms.

(ii) In the uranium pile of nuclear reactors.

(iii) For the production of deuterium.

Heavy Water in India : India needs heavy water for her nuclear reactors. It is being prepared in sufficient quantities about 15000 kg per year at Nangal fertiliser factory (Punjab) since 1962, but more units are being set up at Rourkela, Trombay, Neyveli and Naharketiya.

Typical Questions with Answers

1. *'H' is more powerful reducing than H_2.*

Ans. The reduction potential of atomic hydrogen (H) (–2·10 V) is greater than molecular hydrogen (H_2) (0·60 V). Hence atomic hydrogen is more reducing than molecular hydrogen.

2. *H_2 is not used for the reduction of transition metal oxides. Why ?*

Ans. Hydrogen is not used for the reduction of transition metal oxides because it forms interstitial hydrides.

3. *Copper does not give H_2 with H_2SO_4. Explain.*

Ans. Since copper is below hydrogen in Electrochemical series.

4. *Hydrogen is used as a rocket fuel. Explain.*

Ans. Since it is the lightest gas. A small amount of liquid H_2 will produce larger volume of gaseous H_2. It is a highly combustible substance and its heat of combustion is very high (68·4 kcal/mole).

5. *H_2 can be collected at cathode and anode both. Explain.*

Ans. In NaH, H_2 behaves as electronegative. Hence, when fused NaH is electrolysed, then H_2 is evolved at anode.

Electrolysis

$$\underset{\text{Fused}}{NaH} \rightarrow Na^+ + H^-$$

Cathode $Na^+ + e \rightarrow Na$
Anode $2H^- \rightarrow H_2 + 2e$

In HCl, H_2 behaves as electropositive. Hence, when it is electrolysed then H_2 is evolved at cathode.

$$HCl \rightarrow H^+ + Cl^-$$

Cathode $2H^+ + 2e \rightarrow H_2$

Thus H_2 can be collected at cathode and anode both.

Questions

Long Type Questions

1. Discuss the position of Hydrogen in periodic table. **(M. U. 1975 A)**

2. Mention the various methods of manufacture of hydrogen and give its important uses.

3. (a) How pure hydrogen is obtained ?
   (b) What happens when
      (i) steam is passed over red hot iron,
      (ii) zinc reacts with sodium hydroxide,
      (iii) dil. HNO_3 reacts with Mg,
      (iv) hydrogen is passed over red hot CuO.

4. What do you know about ortho and para hydrogen ? How is deuterium obtained ? **(B. U. 1976 A)**

5. What is nascent hydrogen ? What are the theories of nascent hydrogen ?

6. How is atomic hydrogen prepared and what are its properties ?

7. What is heavy water ? How it is manufactured on large scale ? **(B. U. 1975 A)**

What happens when heavy water reacts with
(a) Na, (b) HCl, (c) P_2O_5, (d) NH_4Cl ?
Give two uses of heavy water.

Short Type Questions

8. Explain the following :
   (a) The nascent hydrogen is more reactive than molecular hydrogen.
   (b) Copper does not give hydrogen with H_2SO_4.
   (c) Hydrogen is used in rocket fuel.

9. Explain with two examples that hydrogen can be placed in IA (alkali metals) and VIIA (halogen) of the periodic table.

10. Write notes on—

(a) Hydrogenation of oils and fats (b) Nascent hydrogen (B. U. 1975 A)
(c) Occuluded hydrogen (d) Atomic hydrogen (e) Active hydrogen
(f) Heavy hydrogen (g) Occulusion (h) Isotopes of hydrogen.
(B. U. 1976 A)

11. **Fill in the blank :**

(a) When the spins are in the same direction the molecule is called———hydrogen.
(b) Tritium is a———hydrogen.
(c) Deuterium is an———of hydrogen.
(d) Heavy water is———oxide.
(e) Hydrogen is occuluded by heated———
(f) Hydrogen contains———electron,———proton.

12. **Match the Column A with B.**

A	B
1. Deuterium	(a) radioactivities hydrogen.
2. Deuterium oxide	(b) H_2 is used.
3. Tritium	(c) contains one proton and one neutron.
4. In Hydrogenation of oils and fats	(d) is used in nuclear reactor.

13. **State Whether the following statement is true or false:**

(a) Copper reacts with H_2SO_4 to give H_2.
(b) Zinc is boiled with $NaOH$ to give H_2.
(c) The nascent hydrogen is more reactive than molecular hydrogen.
(d) Deuterium is known as heavy water.
(e) Hydrogen resembles with IA elements as well as VIIA (Halogen) elements.
(f) Heavy water is used in nuclear reactors.
(g) The electronic configuration of heavy hydrogen is $1s^2$.
(h) One mole of iron reacts with excess of steam to give 4 moles of H_2.

Select and write the correct answer :

14. Which of the following does not give H_2 with dil. H_2SO_4 ?
(1) Zn, (2) Fe, (3) Cu, (4) Al.

15. Which of the following method is not suitable for the preparation of H_2 in the laboratory ?
(1) Na in H_2O, (2) Steam on red hot iron,
(3) Cu with H_2O, (4) more than one.

16. The most dangerous method of preparing hydrogen would be by the action of HCl and
(a) Zn (2) Fe (3) K (4) Al.

17. H_2 from HCl can be prepared from :
(1) Mg (2) Cu (3) P (4) Hg. (CPMT 1980)

18. Metals like platinum and palladium can absorb large volume of hydrogen under special conditions. Such absorbed hydrogen by the metals is known as :
(1) Absorbed hydrogen, (2) Occuluded hydrogen.
(3) Reactive hydrogen, (4) Atomic hydrogen.
(CPMT 1978)

19. Hydrogen is evolved by the action of cold dilute HNO_3 on
(1) *Fe*, (2) *Cu*, (3) *Mn*, (4) *Al*. **(IIT 1978)**

20. Which is the lightest gas ?
(1) Helium, (2) Hydrogen, (3) Nitrogen, (4) Oxygen. **(CPMT 1972)**

21. Which of the following can absorb large volumes of hydrogen gas ?
(1) Finely divided platinum,
(2) Finely divided nickel,
(3) Colloided solution of palladium,
(4) Colloided ferric hydroxide. **(NCERT 1980)**

22. The nuclei of tritium (H_3) atom would contain............neutrons.
(1) 1, (2) 2, (3) 3, (4) 4.

23. Heavy water is
(1) $H_2{}^{18}O$, (2) D_2O,
(3) water obtained by repeated distillation,
(4) water at 4°C. **(IIT 1983)**

24. When the same amount of zinc is treated separately with excess of H_2SO_4 and excess of *NaOH*, the ratio of volume of H_2 evolved is :
(1) 1 : 1, (2) 1 : 2, (3) 2 : 1, (4) 9 : 4.

25. Which of the following reacts with hydrogen violently ?
(1) F_2, (2) Cl_2, (3) Br_2, (4) I_2.

26. Tritium is an isotope of
(1) Hydrogen, (2) Tellurium, (3) Titanium, (4) Tantalum. **(BHU 1979)**

27. The boiling point of Heavy water is
(1) less than ordinary water, (2) equal to ordinary water,
(3) slightly higher than ordinary water,
(4) none.

CHAPTER 6

WATER (H_2O) AND HYDROGEN PEROXIDE (H_2O_2)

1. WATER (H_2O)

6.1. Occurrence

Water occurs in nature in the form of (i) a solid—ice, snow etc, (ii) a liquid—water and (iii) vapours—water vapours in the atmosphere, steam, etc.

About 75 per cent of the surface of the earth is covered by water either in the form of oceans, rivers and lakes or as ice on the tops of mountains and in arctic regions. It is also an essential constituent of all animal and vegetable matter. It is present to the extent of about 70 per cent in human body and 50 to 75 per cent in land plants.

6.2. Natural Water

Pure water is never found in nature due to its great solvent action. Natural water contains a number of impurities depending upon its source and have, therefore, been classified as (a) Rain water, (b) River water, (c) Spring water, (d) Well water, (e) Mineral water, (f) Sea water etc.

6.3. Hard and Soft Water

(i) *Hard water* is that which does not give lather or froth with soap until much of it has been used up. (ii) *Soft water* is that which easily forms lather or froth with soap and does not form a precipitate with it.

Hardness of water is due to the presence of bicarbonates, chlorides, sulphates of magnesium and calcium. Ordinary soap is mostly sodium stearate. When it is dissolved in hard water, a precipitate of calcium and magnesium stearates is formed due to the reaction of calcium and magnesium salts present in water with sodium stearate of the soap. No lather is, therefore, obtained till all the calcium and magnesium ions have been removed. Hard water is thus unsuitable for washing.

$$\underset{\text{Sodium stearate}}{2C_{17}H_{35}COONa} + MgSO_4 \rightarrow \underset{\text{Magnesium stearate}}{(C_{17}H_{35}COO)_2Mg} + Na_2SO_4$$

6.4 Hardness of Water

(i) **Temporary Hardness of Water** : It is due to the presence of bicarbonates of calcium and magnesium;

$$M(HCO_3)^2\ (M = Mg^{+2}, Ca^{+2}).$$

(ii) **Permanent Hardness of Water** : It is due to the presence of chlorides and sulphates of calcium and magnesium;

$$MCl_2, MSO_4 \ (M = Mg^{+2}, Ca^{+2}).$$

6.5. Degree of Hardness

The degree of hardness is always expressed as equivalent of calcium carbonate though it may actually be caused by other salts. Hence it may be defined as "the number of parts by weight of calcium carbonate (or its equivalent) present per 100,000 (i.e. one million) parts by weight of water". Thus if water contains 60 parts of $MgSO_4$ per million parts of water, its degree of hardness would be expressed as 50 parts of $CaCO_3$ per million parts of water (i.e. 50 p.p.m.). It is due to the fact that 1 mole (i.e. 120 gm) of $MgSO_4$ is equivalemt to 1 mole (i.e. 100 gm) of $CaCO_3$.

One gm mole of $MgSO_4$	one gm mole of $CaCO_3$
$24+32+64$	$40+12+48$
$=120$ gm	$=100$ gm
$=60$ gm	$=50$ gm.

A fresh water has degree of hardness ranging from 10 to 500 parts of $CaCO_3$ per million parts of water.

6.6. Removal of Temporary Hardness

(i) *By boiling* : When temporary hard water is boiled then insoluble $MgCO_3$ and $CaCO_3$ is obtained. It is filtered out. Thus hardness of water is removed.

$$M(HCO_3)_2 \rightarrow MCO_3\downarrow + CO_2\uparrow + H_2O \ (M = Mg^{+2}, Ca^{+2}).$$

(ii) *By Clark's process* : When temporary water is boiled with slaked lime, $Ca(OH)_2$, then bicarbonates of calcium and magnesium is converted into insoluble carbonates.

$$\underset{\text{soluble}}{Ca(HCO_3)_2} + \underset{\text{slaked lime}}{Ca(OH)_2} \rightarrow \underset{\text{insoluble}}{2\,CaCO_3} + 2H_2O$$

$$\underset{\text{soluble}}{Mg(HCO_3)_2} + \underset{\text{slaked lime}}{Ca(OH)_2} \rightarrow \underset{\text{insoluble}}{MgCO_3 + CaCO_3} + 2H_2O$$

(iii) *By distillation* : It is also removed by distillation.

(iv) *By addition of washing soda* : Hard water can be softened by the addition of sodium carbonate (washing soda) as it will precipitate the insoluble calcium and magnesium salts as carbonates.

$$Ca(HCO_3)_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow\ 2NaHCO_3$$

Removal of Permanent Hardness of Water :

(i) *By washing soda* : Washing soda on being boiled with hard water removes both temporary and permanent hardness.

$$MCl_2 + Na_2CO_3 \rightarrow MCO_3 + 2NaCl$$
$$MSO_4 + Na_2CO_3 \rightarrow MCO_3 + Na_2SO_4 \ (M = Mg^{+2}, Ca^{+2})$$

(ii) *By Permutit* : Permutit is an artificially prepared hydrated sodium aluminium silicate ($Na_2Al_2Si_2O_8.H_2O$). When hard water is passed through it, the sodium ion in this compound is replaced by divalent calcium and magnesium.

$$Na_2Al_2Si_2O_8+CaCl_2 \rightleftharpoons CaAl_2Si_2O_8+2NaCl$$

The reaction being reversible and permutit can be regenerated by treatment with concentrated soduim chloride.

$$CaAl_2Si_2O_8+2NaCl \rightarrow Na_2Al_2Si_2O_8+CaCl_2$$

In practice permutit is kept in a cylindrical tank and hard water is allowed to percolate through downwards, at the bottom soft water is collected which is taken out through the outlet. The method is very useful in removing both temporary and permanent hardness of water. The process is very cheap.

(iii) *Ion Exchange Resins* (1935) have also become very popular as water softner these days. Hard water is first passed through an acid resin (H. Resin) which absorbs the cations of the salt Mg^{+2}, Ca^{+2} present in hard water.

$$\underset{\text{Cation exchanger}}{2RH} + Ca^{++} \rightarrow R_2Ca+2H^+$$

$$\underset{\text{Cation exchanger}}{RH} + Na^+ \rightarrow RNa+H^+$$

The anions which are present in the form of acids are then removed by passing through a base-resin.

$$\underset{\text{(Base resin)}}{\text{Resin}} + NH_2+H^++Cl^- \rightarrow \text{Resin}-NH_3Cl$$

The water which has passed through such an ion exchange unit does not contain any ions and is as good as distilled water.

Resins can be easily regenerated.

(iv) *Calgon* : It is the commercial name given to sodium hexametaphosphate, $Na_2\,[Na_4\,(PO_3)_6]$.

This does not precipitate calcium or magnesium but forms as salt containing these inside the complex.

$$Na_2[Na_4(PO_3)_6]+2CaSO_4 \rightarrow Na_2[Ca_2(PO_3)_6]+2Na_2SO_4$$

$$2M^{++}+Na_4[(PO_3)_6] \rightarrow M_2(PO_3)_6+4Na^+.$$

This method is very widely used in softening water for boilers and laundry purposes.

Another substitute of calgon commonly used as water softner is **versena** which is a polyamino acid and works in the same way as calgon.

6.8. Physical Properties

(a) Pure water is transparent, odourless, and tasteless liquid.
(b) It freezes at 0°C and boils at 100°C at 760 mm pressure.

(c) It is a poor conductor of electricity. A few drops of an acid or an alkali make it capable of being electrolysed.

(d) Its density is maximum at 4°C. 1 ml of water weighs 1 gm at this temperature.

(e) Its latent heat of fusion and vaporisation are 80 cal/gm and 537 cal/gm respectively. These abnormally high values are due to hydrogen bonding in solid and liquid states.

(f) It is neutral to litmus.

6.9. Chemical Properties

(a) *Stabiliy* : Water is very stable compound and is not appreciably decomposed even at very high temperatures.

$$2H_2O \rightarrow 2H_2+O_2$$

The stability of water is due to the high value of its heat of formation.

$$2H_2+O_2 \rightarrow 2H_2O(l)+68{\cdot}4 \text{ k cal/mole.}$$

(b) *Reaction with Metals* :

(i) $2M+2H_2O \xrightarrow{\text{cold}} 2MOH+H_2\,(M=Na,\ K)$

(ii) $\underset{\text{Red hot}}{3Fe} + \underset{\text{steam}}{4H_2O} \longrightarrow Fe_3O_4+4H_2$

(iii) Metals such as copper, silver, gold, mercury and tin do not decompose water.

(c) *Reaction with Non-metals* :

(i) $\underset{\text{Red hot}}{C} + \underset{\text{Steam}}{H_2O} \rightarrow \underbrace{CO + H_2}_{\text{Water gas}}$

(ii) $\underset{\text{Red hot}}{Si} + \underset{\text{Steam}}{2H_2O} \rightarrow SiO_2 + 2H_2$

(d) *Reaction with Metallic exides* : It combines with certain oxides of metals, such as sodium oxide and calcium oxide to form bases.

$$Na_2O+H_2O \rightarrow 2NaOH$$
$$CaO+H_2O \rightarrow Ca(OH)_2$$

(e) *Reaction with Non-metallic oxides* : It combines with certain non-metallic oxides producing acids.

$$SO_3+H_2O \rightarrow H_2SO_4$$
$$P_2O_5+H_2O \rightarrow \underset{\text{Metaphosphoric acid}}{2HPO_3}$$

(f) Reaction with *Metallic Hydrides, Nitrides, Phosphides and Carbides* :

These compounds react with water with the evolution of hydrogen, ammonia, phosphine and hydrocarbons.

$$CaH_2+2H_2O \rightarrow Ca(OH)_2+2H_2$$
$$AlN+3H_2O \rightarrow Al(OH)_3+NH_3$$
$$Ca_3P_2+6H_2O \rightarrow 3Ca(OH)_2+2PH_3$$
$$CaC_2+2H_2O \rightarrow Ca(OH)_2+\underset{\text{acetylene}}{C_2H_2}$$
$$Al_4C_3+12H_2O \rightarrow 4Al(OH)_3+\underset{\text{methane}}{3CH_4}$$

(g) *Formation of hydrates* : It combines with a number of salts during crystallisation to form hydrates. Some examples of salts containing water of crystallisation are $CuSO_4.5H_2O$ (Blue vitriol), $MgSO_4.7H_2O$ (Epsom salt) and $Na_2CO_3.10H_2O$ (washing soda).

These waters are known as *water of crystallisation.*

(h) *Produces ionisation* : When acids, bases and salts are dissolved in water, they dissociated to produce ions.

$$HCl \rightarrow H^+ + Cl^-; \quad KOH \rightarrow K^+ + OH^-$$
$$NaCl \rightarrow Na^+ + Cl^-$$

(i) *Hydrolysis* : It brings about partial hydrolysis of salts of weak acids or weak bases. Thus, a solution of sodium carbonate is alkaline whereas a solution of copper sulphate is acidic.

$$Na_2CO_3+2H_2O \rightleftharpoons \underset{\substack{\text{(strong)}\\ \text{base}}}{2NaOH} + \underset{\substack{\text{(weak)}\\ \text{acid}}}{H_2CO_3}$$
$$CuSO_4+2H_2O \rightleftharpoons \underset{\substack{\text{(weak)}\\ \text{base}}}{Cu(OH)_2} + \underset{\substack{\text{(strong)}\\ \text{acid}}}{H_2SO_4}$$

6.10. Composition

Steam contains its own volume of hydrogen and half volume of oxygen at S.T.P.

$$H_2O \rightarrow H_2+\tfrac{1}{2}O_2$$

6.11. Uses

Water is used in (a) domestic operations such as cooking, bathing, drinking, and washing etc., (b) irrigation, (c) power generation, (d) chemical industries, (e) sterilisation, (f) laboratory uses etc.

2. HYDROGEN PEROXIDE (H_2O_2)

6.12. Occurrence

It is found in atmosphere in negligible quantity. It is possibly obtained by the action of ultraviolet rays on water vapour and oxygen.

6.13. Methods of Preparation

(i) *From Barium Peroxide* (Laboratory method) : When ice cold dil. H_2SO_4 is added to an ice cold suspense of hydrated barium peroxide, hydrogen peroxide is obtained. The precipitated barium sulphate ($BaSO_4$) is filtered out. The success of the reaction depends upon good stirring, efficient cooling and never having an excess of barium peroxide.

$$BaO_2.8H_2O+H_2SO_4 \rightarrow BaSO_4 \downarrow +H_2O_2+8H_2O.$$

The solution of H_2O_2 obtained above, is only 20%.

(ii) *E. Merck's process* : Hydrogen peroxide is obtained by adding sodium peroxide to well cooled dil. H_2SO_4 (20%).

$$Na_2O_2+H_2SO_4 \rightarrow Na_2SO_4+H_2O_2$$

(iii) *Electrolytic process* : This is the modern and the commercial method of preparation of H_2O_2. It consists of electrolysis of 50% H_2SO_4 or ammonium bisulphate in a diaphragm cell at low temperature. Perdisulphuric acid or ammonium perdisulphate is liberated at anode with dil. H_2SO_4 under reduced pressure.

Reactious : (i) $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$

At Anode : $2HSO_4^- \rightarrow \underset{\text{Perdisulphuric acid}}{H_2S_2O_8} + 2e$

$H_2S_2O_8+2H_2O \rightarrow 2H_2SO_4+H_2O_2$

At Cathode : $2H^+ + 2e \rightarrow H_2$

(ii) $NH_4HSO_4 \rightarrow H^+ + NH_4SO_4^-$

At Anode : $2NH_4SO_4^- \rightarrow (NH_4)_2S_2O_8+2e$

$(NH_4)_2S_2O_8+H_2SO_4 \rightarrow H_2S_2O_8+(NH_4)_2SO_4$

$H_2S_2O_8+2H_2O \rightarrow 2H_2SO_4+H_2O_2$

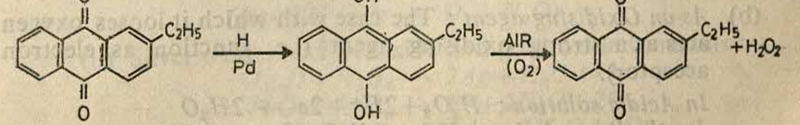
At Cathode : $2H^+ + 2e \rightarrow H_2$

A dilute solution (30-35%) of H_2O_2 is obtained.

(iv) *Auto oxidation process* : This is the most recent process being used in U. S. A. In this method anthraquinone derivative is dissolved in organic solvent and reduced by H_2 in the presence of *Pd* as a catalyst. This on oxidation by air regenerates anthraquinone derivative along with H_2O_2.

2-Ethyl-Anthraquinone $+H_2 \xrightarrow[Pd]{}$ 2-Ethyl-Anthraquinol

$\underset{\text{(air)}}{O_2} \longrightarrow$ 2-Ethyl-Anthraquinone $+H_2O_2$



6.14. Concentration of Dilute solution of Hydrogen peroxide

The solution of hydrogen peroxide obtained by any of the methods described above is dilute and is concentrated as described below :

Concentration of Hydrogen peroxide : Hydrogen peroxide is concentrated as below :

(a) By carefully evaporating it in platinum vessel at 70°C. The concentration is thereby raised to 60%. By further evaporating over conc. H_2SO_4 in a vacuum desicator cooled in a freezing mixture 95% H_2O_2 may be obtained. The last traces of water may be removed by freezing hydrogen peroxide in a freezing mixture of solid CO_2 and either separating the crystals of H_2O_2 and remelting them.

(b) A better way of concentrating the solution of H_2O_2 is by distilling it under reduced pressure (Wolffente in 1894). The temperature is at first kept about 50° when water passes over and as soon as it rises to 70°C, H_2O_2 distils over. This is 99·1% pure.

6.15. Physical Properties

(a) Anhydrous H_2O_2 is a colourless liquid with no odour. It has a bitter taste. It has, however, a bluish tinge in thick layers.

(b) It is readily miscible with water, alcohol and ether.

(c) Its specific gravity is 1·44. Hence, it is about one and a half times heavier than water.

(d) Its melting point is 0·9°C. Its boiling point cannot be determined experimentally since it decomposes below its boiling point.

6.16. Chemical Properties

The chemical properties of hydrogen peroxide can be studied under the headings : (a) stability, (b) as oxidising agent, (c) as reducing agent, (d) as acid, (e) as bleaching agent.

(a) *Stability* : Hydrogen peroxide is an unstable liquid. It decomposes on heating or at Room Temperature and Pressure (R.T.P.) The decomposition is accelerated by manganese dioxide, organic matter, light etc.

$$2H_2O_2 \rightarrow 2H_2O+O_2$$

(b) *As an Oxidising agent* : The case with which it looses oxygen acts as a strong oxidising agent] (i.e. function as electron acceptor).

In Acidic solution : $H_2O_2+2H^++2e \rightarrow 2H_2O$

In Alkaline solution : $HO_2^-+H_2O+2e \rightarrow 3OH^-$

The followings are some important examples :

(i) It oxidises *Potassinm iodide to Iodine* :

$$\begin{array}{rcl} H_2O_2 & \rightarrow & H_2O+\text{'}O\text{'} \\ 2KI+H_2SO_4+O & \rightarrow & K_2SO_4+H_2O+I_2 \\ \hline 2KI+H_2SO_4+H_2O_2 & \rightarrow & K_2SO_4+2H_2O+I_2 \\ 2I^-+2H^++H_2O_2 & \rightarrow & 2H_2O+I_2 \end{array}$$

(ii) It oxidises *Lead sulphide into Lead sulphate* :

$$\begin{array}{rcl} [H_2O_2 & \rightarrow & H_2O+O]\times 4 \\ PbS+4O & \rightarrow & PbSO_4 \\ \hline PbS+4H_2O_2 & \rightarrow & PbSO_4+4H_2O \end{array}$$

(iii) It oxidises *Sodium sulphite to Sodium sulphate* :

$$\begin{array}{rcl} H_2O_2 & \rightarrow & H_2O+O \\ Na_2SO_3+O & \rightarrow & Na_2SO_4 \\ \hline Na_2SO_3+H_2O_2 & \rightarrow & Na_2SO_4+H_2O \\ (SO_3^{-2}+H_2O_2 & \rightarrow & SO_4^{-2}+H_2O) \end{array}$$

(iv) It oxidises *Ferrous sulphate to Ferric sulphate* :

$$\begin{array}{rcl} H_2O_2 & \rightarrow & H_2O+\text{'}O\text{'} \\ 2FeSO_4+H_2SO_4+O & \rightarrow & Fe_2(SO_4)_3+H_2O \\ \hline 2FeSO_4+H_2SO_4+H_2O_2 & \rightarrow & Fe_2(SO_4)_3+2H_2O \\ (2Fe^{+2}+2H^++H_2O_2 & \rightarrow & 2Fe^{+++}+2H_2O) \end{array}$$

(v) It oxidises Ferrocyanide to Ferricyanide :

$$2K_4[Fe(CN)_6]+H_2SO_4+H_2O_2 \rightarrow 2K_3[Fe(CN)_6] + K_2SO_4+2H_2O$$

$$[2Fe(CN)_6^{-4}+H_2O_2+2H^+ \rightarrow 2Fe(CN)_6^{-3}+2H_2O]$$

In *alkaline medium* its oxidising property is rapid. It oxidises manganeous salt in alkaline medium to manganese dioxide and chromic salt to chromate.

$$\begin{array}{lrcl} & Mn^{++}+H_2O_2+2OH^- & \rightarrow & MnO_2+2H_2O \\ & 2Cr(OH)_3+3H_2O_2+4OH^- & \rightarrow & 2CrO_4^{-2}+8H_2O \\ \text{or} & 3Cr^{+3}+3H_2O_2+10OH^- & \rightarrow & 2CrO_4^{-2}+8H_2O \end{array}$$

(c) *As reducing agent* : It accepts oxygen from various oxidising agents to evolve O_2 and thus reduces them (i.e. functions as an electron donor).

$$H_2O_2 \rightarrow O_2+2H^++2e$$

The following are some important examples :

(i)

$$\begin{array}{rcl} H_2O_2 & \rightarrow & H_2O+O \\ O_3 & \rightarrow & O_2+O \\ O+O & \rightarrow & O_2 \\ \hline H_2O_2+O_3 & \rightarrow & H_2O+2O_2 \\ (O_3+2H^++2e & \rightarrow & O_2+H_2O) \end{array}$$

(ii) Silver oxide, lead peroxide and gold oxide to metals :

$$\begin{array}{rcl} Ag_2O+H_2O_2 & \rightarrow & 2Ag+H_2O+O_2 \\ PbO_2+H_2O_2 & \rightarrow & Pb+2H_2O+2O_2 \\ Au_2O_3+H_2O_2 & \rightarrow & 2Au+3H_2O+3O_2 \end{array}$$

(iii) Halogens to their halogen acids :

$$Br_2+H_2O_2 \rightarrow 2HBr+O_2$$
$$(Br_2+H_2O_2 \rightarrow 2Br^-+2H^++O_2)$$

(iv) Acidified potassium permanganate ($KMnO_4$) violet to colourless manganeous salts :

$$2KMnO_4+3H_2SO_4 \rightarrow K_2SO_4+2MnSO_4+3H_2O+5\text{'}O\text{'}$$
$$[H_2O_2+O \rightarrow H_2O+O_2]\times 5$$
$$\overline{3KMnO_4+3H_2SO_4+5H_2O_2 \rightarrow K_2SO_4+2MnSO_4+8H_2O+5O_2}$$
$$\text{or} \quad (2MnO_4^{-1}+6H^++5H_2O_2 \rightarrow 2Mn^{+2}+8H_2O+5O_2)$$

(v) *Alkaline Potassium ferricyanide to ferrocyanide :*

$$2K_3[Fe(CN)_6]+H_2O_2+2KOH \rightarrow 2K_4[Fe(CN)_6+2H_2O+O_2$$
$$[2Fe(CN)_6^{-3}+2OH^-+H_2O_2 \rightarrow 2Fe(CN)_6^{-4}+2H_2O+O_2]$$

(d) *As Acid* : It acts as an acid because it gives CO_2 with sodium carbonate. It forms one acid salt ($NaHO_2$) and one normal salt an (Na_2O_2) with sodium hydroxide.

Hence it is a dibasic acid.

$$Na_2CO_3+H_2O_2 \rightarrow Na_2O_2+CO_2+H_2O$$
$$NaOH+H_2O_2 \rightarrow NaHO_2+H_2O$$
$$2NaOH+H_2O_2 \rightarrow Na_2O_2+2H_2O$$

(e) *As Bleaching agent* : It acts as a bleaching agent. It bleaches due to oxidation (Nascent oxygen) and bleaching is permanent.

$$H_2O_2 \rightarrow H_2O+\text{'}O\text{'}$$

Coloured substance $+$'O' $\rightarrow$ colourless

6.17. Test

(i) It gives iodine with potassium iodide which turns starch paper blue.

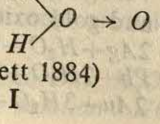
$$2KI+H_2O_2 \rightarrow 2KOH+I_2$$
$$\text{starch} + I_2 \rightarrow \text{blue}$$

(ii) To the dilute solution of H_2O_2, acidified $K_2Cr_2O_7$ solution was added followed by ether. The etheral layer turns light blue which indicates the presence of H_2O_2.

$$Cr_2O_7^{-2}+2H^++4H_2O_2 \rightarrow \underset{\text{blue in ether}}{2CrO_5} + 5H_2O$$

6.18. Constitution of H_2O_2

From analytical data and molecular weight determination its molecular formula comes to H_2O_2. The two possible structural formulae are :



$H-O-O-H$

(Kingzett 1884) (Baeyer 1900)
I II

Evidence in Favour of Formula I.

Hydrogen peroxide is an oxidising agent and one oxygen atom is lost from the molecule. It is possible from I only (Kingzett 1884).

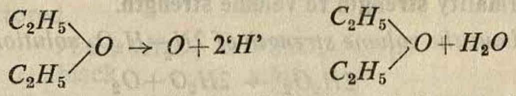
Evidence in Favour of Formula II.

(i) As H_2O_2 is a weak dibasic acid, it forms two series of salts e.g. $NaO—OH$ and $NaO—ONa$. It shows the presence of two hydroxyl groups in molecule as in II.

(ii) H_2O_2 reacts with diethyl sulphate forming diethyl peroxide which on reduction yields ethyl alcohol. This can again be explained from II only.

$$OH-OH+(C_2H_5)_2SO_4 \rightarrow C_2H_5-O-O-C_2H_5+H_2SO_4$$
$$C_2H_5-O-O-C_2H_5+2H \rightarrow 2C_2H_5OH$$

On the other hand formula I will give diethyl ether.

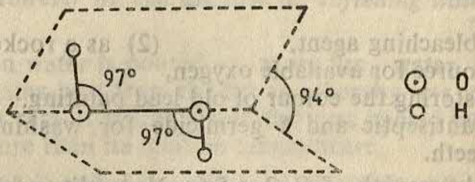


$$\begin{matrix}C_2H_5\\ C_2H_5\end{matrix}\!\!>O \rightarrow O+2\text{'}H\text{'} \qquad \begin{matrix}C_2H_5\\ C_2H_5\end{matrix}\!\!>O+H_2O$$

(iii) H_2O_2 with excess of chlorosulphonic acid gives perdisulphuric acid. It shows that the structure of hydrogen peroxide should be II and not I.

(iv) Other investigations like infra red absorption spectra, dipole moment etc. also confirm dihydroxyl formula II.

The angle between $O-H$ and $O-O$ bond by these physical data comes to 97°. Bond length $O-H$ is $1{\cdot}01 \pm 0{\cdot}03$ A° and $O-O$ is $1{\cdot}48 \pm 0{\cdot}02$ A° respectively.



An aqueous solution of H_2O_2 is now considered to be a mixture of both the forms in tautomeric equilibrium.

6.19. Strength of Hydrogen Peroxide

An aqueous solution of hydrogen peroxide is sold in the market under specifications of volumes e.g. 10 volumes, 20 volumes or 30 volumes. These signify that one ml of 10 volumes solution of H_2O_2 would give 10 ml of O_2 at S.T.P. on decomposition. Further 20 volumes solution of H_2O_2 means 1 ml of this solution will give on heating 20 ml of O_2 at S.T.P.

(a) Volume strength to normality strength :

1. *Calculate the normality of* 20 *volumes of* H_2O_2 *solution.*

Sol.

$$\begin{array}{ll} 2H_2O_2 \rightarrow & 2H_2O+O_2 \\ & \qquad\quad 22400 \text{ c.c. at S.T.P.} \end{array}$$

or 22400 c.c. O_2 at S.T.P. is given out from 68 gm H_2O_2

$$20 \text{ c.c. } O_2 \text{ at S.T.P. is } \frac{68\times 20}{22400}=0{\cdot}0607 \text{ gm.}$$

$$\text{Normality : } = \frac{\text{Wt. in gm}\times 1000}{\text{eq. wt. of } H_2O_2\times \text{vol (ml)}}$$

$$=\frac{0{\cdot}0607\times 1000}{17\times 1}=\frac{60{\cdot}7}{17}=3{\cdot}57.$$

Hence normality of 20 volumes of H_2O_2 solution is 3·57. Ans.

(b) Normality strength to volume strength.

2. *Find out the volume strength of* $2N-H_2O_2$ *solution.*

Sol.

$$\begin{array}{ll} 2H_2O_2 \rightarrow & 2H_2O+O_2 \\ 2\times 34\ g & 22400 \text{ c.c. at S.T.P.} \\ 2\times 2000 \text{ c.c. } N & 22400 \text{ c.c. } O_2 \text{ at S.T.P.} \end{array}$$

$$1 \text{ c.c. } 2N\ H_2O_2 \text{ gives } \frac{22400}{2000} \text{ c.c. } O_2 \text{ at S.T.P.}$$

$$=11{\cdot}2 \text{ c.c. } O_2 \text{ at S.T.P.}$$

Hence volume strength of H_2O_2 is 11·2.

Note : $1N\ H_2O_2=5{\cdot}6$ Vol. H_2O_2.

6.20. Uses

(1) As a bleaching agent, (2) as a rocket fuel,

(3) as a source for available oxygen,

(4) for restoring the colour of old lead painting.

(5) as an antiseptic and a germicide for washing wounds, ear and teeth.

Note : Vol. strength of $H_2O_2=5{\cdot}6\times$ Normality of H_2O_2.

Typical Questions with Answers

1. *What do you mean by hard water ? Describe the tests you would perform to determine the nature of hardness of a sample of water.*

Ans. For first part see Article 6.3.

To determine the nature of hardness of a sample of water.

(a) When water is boiled in a test tube, then white precipitate is obtained. This indicates the presence of temporary hardness of water.

$$M(HCO_3)_2 \rightarrow MCO_3 \downarrow +H_2O+CO_2 \ (M=Mg^{+2}, Ca^{+2})$$

(b) Filter out the precipitate and add Na_2CO_3 solution to the fiiltrate and boil, then again white precipitate is obtained. This indicates the presence of permanent hardness of water.

$$M^{++} + Na_2CO_3 \rightarrow MCO_3 \downarrow + 2Na^+ \ (M^{++} = Mg^{+2}, Ca^{+2})$$

2. *Explain the following* :

(a) *Hard water is not used for laundry.*

(b) *The colour of old paintings may be restored by* H_2O_2.

Ans. (a) Hard water causes waste of soap, when used for laundry purposes and hence it is not used. For detail see hard water.

(b) The old painting turns black by the action of atmospheric H_2S upon white lead (white paints). When this old oil-painting is washed wlth H_2O_2 then white lead sulphate is obtained. Hence white colour of old oil-painting is restored.

$$\underset{\text{black}}{PbS} + 4H_2O_2 \rightarrow \underset{\text{white}}{PbSO_4} + 4H_2O$$

3. *Show by chemical reactions that* H_2O_2 *is* :

(a) *a dibasic acid* (b) *as an oxidising agent*

(c) *as a reducing agent* (d) *as a bleaching agent.*

Ans. See H_2O_2, Article 6.16.

4. *Account for the following in not more than four sentences* :

(i) *Water can extinguish most fire, but not petrol fire.* **(BIT 1980)**

(ii) *Hardness of water is due to the presence of* Ca^{+2} *and* Mg^{+2} *ions. However we can use lime for softening water.* **(BIT 1981, '82)**

Ans. (i) When water is poured on most fire, water being cooler (at low temp.) gains heat from the fire and thereby gets cooled due to loss of heat. In case of petrol fire, it also gets cooled but remains at higher temperature than its ignition temperature.

(ii) When lime is added in water then insoluble salts of calcium and Mg are formed which are separated by filtration and hard water becomes soft water.

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$$
$$Mg(HCO_3) + Ca(OH)_2 \rightarrow MgCO_3 \downarrow + CaCO_3 \downarrow + 2H_2O.$$

Questions

Long Type Questions :

1. What causes hardness of water and how it is removed ? **(P. U. 1977; B. U. '64 A; Bhag. U. '73 A; R. U. '69 A, '76 S)**

2. Describe the disadvantage of hardness of water. **(R. U. 1964 A)**

3. How would the addition of (a) sodium carbonate, (b) milk of lime, (c) sodium phosphate affect the hardness of water ?
   Give reasons for your answer. (B. U. 1964 A)

4. A sample of water deposits :
   (a) white solid on boiling and gives precipitate with (b) silver nitrate and (c) barium chloride solutions respectively. What inference would you draw in each case ? (P. U. 1970 A; B. U. '67 A)

5. (a) What do you mean by hard and soft water ?
   (b) How hard water is unsuitable for washing ?
   (c) How temporary hardness of water is removed ?

6. (a) What do you mean by degree of hardness of water ?
   (b) How permanent hard water is removed ?

7. What is permutit process of softening water ?
   What happens when
   (a) steam is passed over red hot iron,
   (b) water is added to CaC_2,
   (c) water is added to P_2O_5,
   (d) steam is passed over red hot carbon,
   (e) water reacts with hydrolith.

8. What methods are available for preparing hydrogen peroxide ? How does hydrogen peroxide act as oxidising and reducing agents both ?

9. How H_2O_2 is obtained by electrolytic method ?
   How it is concentrated ? How does H_2O_2 react with
   (a) acidified KI (b) acidified pot. ferrocyanide
   (c) ozone (d) acidified $KMnO_4$ solution.
   (P. U. 1969 A)

10. (a) Give two reactions to show that H_2O_2 acts as oxidising and reducing agents both,
    (b) H_2O_2 acts as bleaching agent,
    (c) H_2O_2 acts as a dibasic acid.

11. Discuss the constitution of hydrogen peroxide.

12. What happens when :
    (a) Calgon reacts with $CaCl_2$,
    (b) $Mg(HCO_3)_2$ reacts with slaked lime,
    (c) H_2O is added to Al_4C_3,
    (d) H_2O_2 reacts with Br_2,
    (e) H_2O_2 reacts with $FeSO_4$ in presence of H_2SO_4,
    (f) H_2O_2 reacts with Na_2CO_3,
    (g) 50% H_2SO_4 is electrolysed ?

13. (a) How will you show that a given liquid is H_2O_2 ?
    (b) Calculate the normality of 20 volumes of H_2O_2 solution.
    (c) Find out the volume strength of $2N-H_2O_2$ solution.

Short Type Questions :

14. Explain the following :
    (1) H_2O_2 gives acidic properties.
    (2) H_2O_2 is a bleaching agent.
    (3) Calgon is used as water softner.
    (4) Hard water is not used in boiler.
    (5) Water is a liquid.
    (6) Distilled water is not used for drinking purpose (AISB 1980)
    (7) H_2O_2 is kept in cold bottles.

15. Write notes on :
    (a) Degree of hardness (b) Clark's process
    (c) Calgon (d) Concentration of H_2O_2.

16. Describe the ion-exchange resin method for the removal of permanent hardness of water.

17. Fill in the blank :

(a) H_2O contains———bond.
(b) Hard water contains———and———cations.
(c) Sodium hexametaphosphate Is known as———.
(d) Water has maximum density at———.
(e) H_2O_2 is a———agent.
(f) H_2O_2 can———and———electrons.
(g) In Clark's process———is used.

18. Fill in the blank and balance :

(a) $Fe + H_2O \longrightarrow Fe_3O_4$———.
(b) $Ca_3P_2 + H_2O \longrightarrow Ca(OH)_2 +$———.
(c) $P_2O_5 + H_2O \longrightarrow$ ———.
(d) $I^- + H_2O_2 +$———$H_2O +$.
(e) $PbS + H_2O_2 \longrightarrow PbSO_4 +$———.
(f) $KMnO_4 + H_2O_2 + \longrightarrow MnSO_4 + O_2 +$———.
(g) $Na_2CO_3 + H_2O_2 \longrightarrow$ ———.

Very Short Type Questions ;

19. Name the cations and anions present in hard water. (CEET 1981)
20. What do you mean by temporary and permanent hardness of water ?
21. What is obtained by the electrolysis of 50% H_2SO_4 ?
22. Why is hydrogen peroxide concentrated at low pressure ?
23. Give two uses of H_2O_2.
24. What happens when slaked lime reacts with
(a) $MgCl_2$ (b) $CaCl_2$.

Select and write the correct answer :

25. For making H_2O_2 in the laboratory,
1. MnO_2 is added to cold dilute H_3PO_4.
2. BaO_2 is added to CO_2 bubbling through cold water.
3. PbO_2 is added to acidified solution of $KMnO_4$.
4. Na_2O_2 is added to boiling water. (CPMT 1972)

26. Which of the following group of ions makes the water hard ?
1. Sodium and bicarbonate
2. Magnesium and nitrate
3. Potassium and sulphate
4. Ammonium and chloride. (CPMT 1972)

27. Zeolite which shows ion-exchange ability
1. is an ion-exchange resin
2. is a closed packed assemblage of silicon and oxygen atom
3. is a sodium alumino silicate
4. can provide H^+ ions in place of Na^+ ions.

28. Which one is not a water softner ?
(1) Slaked lime (2) washing soda (3) calgon (4) $CaSO_4$.

29. In the laboratory H_2O_2 is prepared by the action of :
(1) cold H_2SO_4 on anhydrous CaO_2,
(2) cold H_2SO_4 on hydrated BaO_3,
(3) MnO_2 and cold H_2SO_4,
(4) dil. HCl on MnO_2.

30. Given colourless liquid will be determined whether it is water or not—
(1) By smelting (2) By testing
(3) By adding a pinch of anhydrous $CuSO_4$ (4) Phenolphthalein.

31. A teacher one day pointed out to his students. The peculiar fact that water is unique liquid which freezes exactly at 0°C and boils at exactly 100°C. He asked the students to find the reason for this from the following :

(1) Boiling and freezing temperature of water were used to define a temperature scale.
(2) Liquid water is denser than ice.
(3) Water is a polar molecule.
(4) Water dissolves anything however sparingly the dissolution may be.

32. "Commercial" 10 volume H_2O_2 is a solution with a strength of approximately

(1) 30% (2) 3% (3) 1% (4) 10%

33. Hydrogen peroxide is used as

(1) oxidising agent (2) reducing agent
(2) bleaching agent (4) all the above.

34. Two moles of $KMnO_4$ reacts with excess of H_2O_2 to give :

(1) 2 moles of O_2 (2) 3 moles of O_2
(3) 5 moles of O_2 (4) 6 moles of O_2.

35. H_2O_2 is used to restore the colour of old lead paintings because it converts PbS (black) to :

(1) Pb (2) $PbSO_3$ (3) $PbSO_4$ (4) None.

36. The volume strength of 2N-H_2O_2 solution is

(1) 10 (2) 11·2 (3) 22·4 (4) 15·4.

CHAPTER 7

STUDY OE THE CARBON GROUP OF ELEMENTS

(Elements of Group IV A)

7.1. Periodic Discussion

Group IV A occupies the central part of periodic table. It consists of nine elements divided into IV A and IV B sub-groups. Carbon is the first member of Group IV A; hence all elements of this sub-group are called elements of the carbon family. All are *p*-block elements ($ns^2\ np^2$). In this group, the difference between the two sub-groups are pronounced than in other groups. IV A sub-group consists of normal elements *carbon*, *silicon*, *germanium*, *tin* and *lead*. Carbon and silicon are typical elements of the group. Silicon may be regarded as the bridge element as it shows similarities both with titanium and germanium.

$$ {}_{6}C - {}_{14}Si \begin{cases} {}_{32}Ge - {}_{50}Sn - {}_{82}Pb & \text{IV A} \\ {}_{22}Ti - {}_{40}Zr - {}_{72}Hf - {}_{90}Th & \text{IV B} \end{cases} $$

Element	*Atomic Number*	*Electronic configuration*	*Atomic radius (Å)*	*Ionisation potential (eV)*	*Electro-negativity*	*Melting point 0°C*	*Oxidation number*
C	6	$[He]2s^2 2p^2$	0·77	11·3	2·5	3727	+(2), 4
Si	14	$\boxed{Ne}\ 3s^2 3p^2$	1·11	8·2	1·8	1410	+(2), 4
Ge	32	$\boxed{Ar}\ 3d^{10} 4s^2 4p^2$	1·22	8·1	1·8	937·5	+(2), 4
Sn	50	$\boxed{\quad}\ 4d^{10} 5s^2 5p^2$	1·41	7·3	1·8	231·8	+(2), 4
Pb	82	$[Xe]4f^{14} 5d^{10} 6s^2 6p^2$	1·44	7·4	1·8	327·4	+(2), 4

(i) **Electronic Structure** : All have four electrons ($ns^2\ np^2$) in their outermost shell and thus exhibit the typical group valency of four.

(ii) **Nature** : Carbon and silicon are non-metals, Germanium is a metallic in nature while tin and lead are metals. Carbon and silicon are electronegative while tin and lead are electropositive.

(iii) **Allotropy** : They all exhibit allotropy. Carbon occurs in two crystalline forms diamond and graphite and in several amorphous forms coal, coke, charcoal etc. Silicon occurs in crystalline and amorphous forms, germanium in two crystalline forms. Tin occurs In three allotropic forms—grey tin, white tin and rhomhic tin.

(iv) **Valency** : All are tetravalent elements. They do not normally form M^{4+} ions as their ionisation potentials are very high. They also do not form M^{4-} ions as they possess low electronegativity. They show a covalency of 4 by acquiring sp^3 hybridisation resulting in a tetrahedral structure.

(v) **Ionisation Potential** : They show high ionisation potentials, the value decreases gradually with the rise in atomic number.

(vi) **Eletronegativity** : The electronegativity value do not show a regular gradation.

(vii) **Atomic Volume** : The values for atomic volume increase gradually.

(viii) **Inert Pair Effect** : The inert pair effect shows itself increasingly in the heavier members of the group. There is a decrease in stability of the +4 O. S. and an increase in the stability of the +2 state on descending the group. Thus $Ge(+2)$ exists as a strong reducing agent and $Ge(+4)$ is stable. $Sn(+2)$ and $Pb(+2)$ are ionic and stable but $Sn(+4)$ and $Pb(+4)$ are covalent. The lower valencies are more ionic because the radius of M^{2+} is greater than M^{4+} and according to Fajans' rule, the smaller the ion the greater the tendency to covalency.

(ix) **Formation of Complexes** : The tendency of an element to form complexes is favoured by (a) high charge, (b) small size of its atom and (c) the availability of empty orbitals of suitable energy. Carbon is in the second period and has a maximum of 8 electrons in its outer shell. It resembles like that of inert gas. Carbon compounds are stable and carbon does not form any complexes.

In the tetra-covalent compounds of subsequent elements, there is an availability of empty *d*-orbitals These can, therefore, form complexes and thereby increase their coordination number from 4 to 6. For example—

$$SiF_4 + 2F^- = [SiF_6]^{2-}$$
$$SnCl_4 + 2Cl^- = [SnCl_6]^{2-}$$

(x) **Hydrides** : All these elements form covalent hydrides. Carbon forms a no. of hydrides, silicon and germanium only a limited numbers, whereas tin and lead form only SiH_4 and PbH_4. Thus the tendency of hydride formation decreases from cabon to lead.

(xi) **Halides** : All these elements form covalent tetrachlorides which are liquids at ordinary temperatures e.g. CCl_4, $SiCl_4$, $GeCl_4$,

$SnCl_4$ and $PbCl_4$. The case of hydrolysis increases from CCl_4 to $PbCl_4$.

(xii) Oxides : They all form oxides MO_2. For example CO_2, SiO_2, GeO_2, SnO_2 and PbO_2. CO_2 and SiO_2 are acidic, GeO_2 weakly acidic and SnO_2 and PbO_2 are amphoteric.

(xiii) Density : It increases from carbon to lead.

(xiv) Alkyl Formation : All form tetralkyls e.g. silicon tetra ethyl $Si(C_2H_5)_4$, and lead tetra ethyl $Pb(C_2H_5)_4$.

(xv) Catenation property : The combination between the atoms of the elements is known as catenation property. This property decreases from carbon to lead.

(xvi) Nitrides : All form nitrides. Cyanogen (C_2N_2) is a highly poisonous gas; Si_3N_4, Ge_3N_4 and Sn_3N_4 are solid and stable compounds.

7.2. Carbon

Atomic Number—6 Atomic Weight—12

Electronic configuration—$1s^2\ 2s^2\ 2p^2$

Occurrence : In the free state, carbon occurs in nature as diamond and graphite. In combination with other elements, it occurs as carbon dioxide in the air, as hydrocarbons in petroleum, as a host of organic compounds in vegetable and animal matters and as inorganic compounds like calcium carbonate and magnesium carbonate in sedimentary rocks.

Allothopic forms : Carbon exhibits allotropy. Different allotropic modifications of carbon are known, which can be divided into two classes, viz. (i) the crystalline form and (ii) the amorphous form. The crystalline form is represented by diamond and graphite, while the amorphous form includes various charcoals (wood charcoal, animal charcoal, sugar charcoal, blood charcoal etc.), lamp-black, coke and gas carbon.

Crystalline Allotropes of Carbon : **(a) Diamond.** It naturally occurs in South Africa and some other African states, Brazil, the Ural mountains and at Golconda in India. Diamond which is used as a gem-stone is generally colourless or slightly tinted, but black or dark-coloured varieties, called *carbonado* or *bort* are also available. The weight of precious diamond is expressed in carats (1 carat = 0·200 gm). Some famous diamonds are Kohinoor (106 pyridine and other organic bases). Bone black, thus obtained, contains about 10% carbon and the rest is mainly calcium phosphate and calcium carbonate. The calcium salts are removed by dissolving with hydrochloric acid and the carbon left is known as *ivory black*.

Blood Charcoal : It is obtained from dried blood by a similar process.

Properties : Charcoal is a black porous substance having a density of 1·4 to 1·9. But it floats on water due to the inclusion of large quantities of air in the pores (the apparent density of charcoal is thereby lowered to about 0·2). It is a bad conductor of heat and electricity. It burns in oxygen and fluorine at about 400°C, forming CO and CO_2.

It is not attacked by alkalies, hydrochloric acid, chlorine, bromine, or iodine. It is oxidised to CO_2 by hot conc. H_2SO_4 and HNO_3.

$$C+2H_2SO_4 \rightarrow CO_2+2SO_2+2H_2O$$
$$C+4HNO_3 \rightarrow CO_2+4NO_2+2H_2O$$

It combines with sulphur vapour forming carbon disulphide. $C+2S \rightarrow CS_2$. Many metallic oxides like Fe_2O_3, PbO, ZnO, SnO_2 are reduced to the corresponding metals on heating with charcoal. It also reduces steam and CO_2 at high temperatures to hydrogen and CO repectively.

$$Fe_2O_3+3C \rightarrow 2Fe+3CO;\ CuO+C \rightarrow Cu+CO$$
$$H_2O+C \rightarrow H_2+CO;\ CO_2+C \rightarrow 2CO$$

Charcoal absorbs many gases and decolorises many coloured liquids.

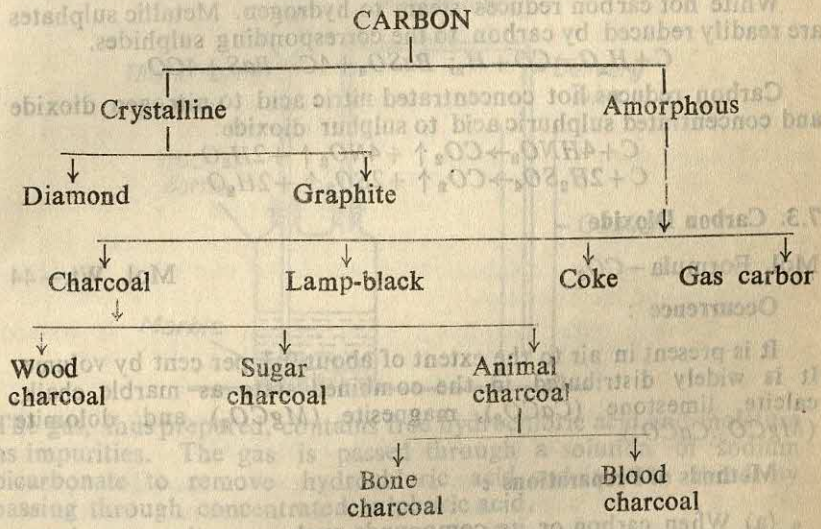
Uses : Charcoal is used as a reducing agent, especially for reducing metallic oxides and also as a decolorsing agent for liquids such as in gas-masks, and for preparing filter-beds. It is an ingredient of gun powder. Ivory black is used as a pigment. Charcoal is also used as a fuel for domestic purposes and also in goldsmith shops.

Coke : It is prepared by the destructive distillation of coal. It contains some impurities like mineral matters and substances containing sulphur and nitrogen. It is a porous substance and does not easily conduct heat or electricity. Coke is used as a fuel and as a reducing agent in metallurgy.

Coal : Coal was formerly regarded as a variety of carbon, but the products of its destructive distillation suggest combination between carbon, hydrogen, oxygen and small amounts of nitrogen and sulphur in coal. It is formed in nature by the slow decay of vegetable matter in limited supply of air and under intense pressure. The character of the coal changes with the time during which the decay has occurred and the successive stages are known as peat, lignite (or brown coal), bituminous coal and anthracite. The percentage of carbon in coal increases and those of hydrogen and oxygen diminish as we pass from the peat to the anthracite stage. The ash left on burning coal is derived from the vegetable and mineral matters present in coal

Activated Charcoal : Specially treated charcoal, which possesses superior absorbent properties to ordinary charcoal is called active or activated charcoal. There are many processes to prepare activated charcoal. In one process, ordinary powdered charcoal is briquetted with wood-tar and a little sodium hydroxide and the granules are heated gradually up to 500°-600°C and the process is concluded by heating in a current of steam at 800°-1000°C. When active charcoal loses its activity, it can be revived by boiling with sodium hydroxide solution, filtering and washing with water. Cocoanut-shells directly give active charcoal on carbonisation. In addition to the uses of charcoal as an absorbing agent for gases and a clarifying agent for liquids, active charcoal is used as a catalyst in many chemical reactions.

Summary of the Allotropic Forms of Carbon



CHEMICAL PROPERTIES OF CARBON

1. Combustion : Carbon, in all its forms, is a combustible material and when burnt in a plentiful supply of air, it gives CO_2, in limited supply of air, the product is CO. In these reactions, large quantities of heat are, in general, produced,

$$C+O_2=CO_2+98{\cdot}05 \text{ Kcal}; \quad 2C+O_2=2CO+52{\cdot}84 \text{ Kcal}.$$

2. Reaction with Non-Metals : When heated in an atmosphere of hydrogen at high temperatures (450°C) and pressures (250 atmos.) carbon combines with hydrogen, giving hydrocarbons like CH_4, C_2H_2, C_2H_4 etc. It combines with sulphur and nitrogen at high temperature to form carbon disulphide and cyanogen respectively. Carbon readily combines with fluorine to form CF_4. With other halogens, it does not combine directly.

$$2C+H_2\rightleftharpoons C_2H_2;\ C+2S\xrightarrow{1000^\circ C}CS_2;\ 2C+N_2=(CN)_2;\ C+2F_2\rightarrow CF_4$$

3. Reaction with Metals : Formation of carbides—Carbon forms compounds with metals and such binary compounds are called carbides. Thus, when a mixture of lime (CaO) and carbon (coke) dust is strongly heated, calcium carbide (CaC_2) results. Silicon carbide (SiC, also called *carborundum*) is also formed similarly.

$$CaO+3C\rightleftharpoons CaC_2+CO;\ SiO_2+3C\rightleftharpoons SiC+2CO$$

4. Reducing property of carbon : Carbon is a good reducing agent and is widely used as a powerful reductant, especially in metallurgy, since the oxides of many metals are reduced by carbon on heating.

$$ZnO+C\rightarrow Zn+CO;\ PbO+C\rightarrow Pb+CO$$

White hot carbon reduces steam to hydrogen. Metallic sulphates are readily reduced by carbon to the corresponding sulphides.

$$C+H_2O\rightleftharpoons CO+H_2;\ BaSO_4+4C\rightleftharpoons BaS+4CO$$

Carbon reduces hot concentrated nitric acid to nitrogen dioxide and concentrated sulphuric acid to sulphur dioxide.

$$C+4HNO_3\rightarrow CO_2\uparrow+4NO_2\uparrow+2H_2O$$
$$C+2H_2SO_4\rightarrow CO_2\uparrow+2SO_2\uparrow+2H_2O$$

7.3. Carbon Dioxide

Mol. Formula—CO_2 Mol. Wt.—44

Occurrence :

It is present in air to the extent of about 0·3 per cent by volume. It is widely distributed in the combined state as marble, chalk, calcite, limestone ($CaCO_3$), magnesite ($MgCO_3$) and dolomite ($MgCO_3.CaCO_3$).

Methods of Preparations :

(a) When carbon or its compounds such as methane are burnt in excess of air or oxygen, carbon dioxide is produced.

$$C+O_2\rightarrow CO_2$$
$$CH_4+2O_2\rightarrow CO_2+2H_2O$$

This is, however, not a convenient method for the preparation of carbon dioxide.

(b) It is obtained by heating carbonates of heavy metals and bicarbonates.

$$CaCO_3 \rightarrow CaO + CO_2$$
$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

(c) It is also produced by the fermentation of glucose with yeast.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \rightarrow \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

(d) It is obtained by the action of dilute acid (HCl or H_2SO_4) on carbonates and bicarbonates of metals.

$$MgCO_3 + H_2SO_4 \rightarrow MgSO_4 + H_2O + CO_2$$
$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$$

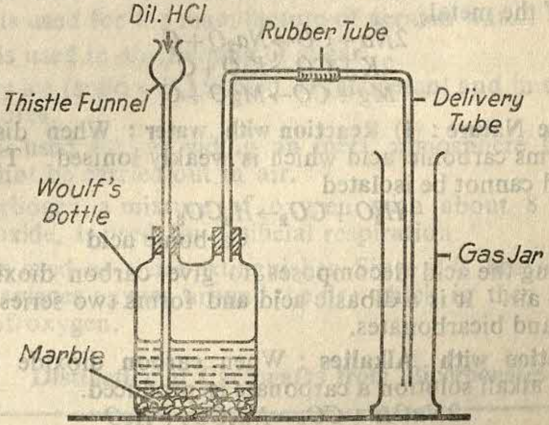
Note : Generally H_2SO_4 is not used.

Laboratory Preparation :

It is prepared in the laboratory by the action of dilute hydrochloric acid on marble ($CaCO_3$).

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$

Pieces of marble are taken in a Woulfe's bottle and the dilute acid is added through the thistle funnel. Carbon dioxide is evolved.



The gas, thus prepared, contains free hydrochloric acid and moisture as impurities. The gas is passed through a solution of sodium bicarbonate to remove hydrochloric acid and is then dried by passing through concentrated sulphuric acid.

Note :· Kipp's apparatus may be used if an intermittent supply of moderate amounts of carbon dioxide is needed in the laboratory.

Physical Properties :

(a) It is a colourless gas with a slightly acidic taste and a faint smell.

(b) It is about 1·5 times as heavy as air (its V. D. being 22 as compared to 14·4 for air).

(c) It is not poisonous. Animals die in it from suffocation because of want of oxygen

(d) It is fairly soluble in water. More of the gas dissolves under increased pressure but effervesces out on releasing it. Aerated water such as soda water and lemonade are solution of carbon dioxide in water under pressure.

(e) It can be liquefied under pressure (60 atmosphere) to a colourless liquid. When the liquid is allowed to evaporate, cooling produced by evaporation freezes it, producing a white snowlike solid, commonly known as *dry ice*. Solid carbon dioxide sublimes at 78·5°C.

Chemical Properties :

(a) **Stability** : It is a very stable compound. Only about 0·3 per cent of it decomposes at 1500°C.

$$2CO_2 \rightarrow 2CO + O_2$$

(b) **Combustibility** : It is an incombustible gas and is a non-supporter of combustion. Metals, such as sodium, potassium and magnesium, however, continue to born in it, producing free carbon and oxide of the metal.

$$2Na + CO \rightarrow Na_2O + C$$
$$2K + CO \rightarrow K_2O + C$$
$$Mg + CO \rightarrow MgO + C$$

(c) **Acidic Nature** : (i) **Reaction with water** : When dissolved in water, it forms carbonic acid which is weakly ionised. The acid is unstable and cannot be isolated

$$H_2O + CO_2 \rightarrow \underset{\text{Carbonic acid}}{H_2CO_3}$$

On heating the acid decomposes to give carbon dioxide which escapes into air. It is a dibasic acid and forms two series of salts, carbonates and bicarbonates.

(ii) **Reaction with Alkalies** : When carbon dioxide is passed through an alkali solution a carbonate is produced.

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

On passing more of carbon dioxide, it is converted into the bicarbonate. $Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$

The milkiness disappears when more of carbon dioxide is passed through it. This is due to thc formation of calcium bicarbonate which is soluble is water.

(iii) **Reaction with Basic Oxides** : Being an acidic oxide, it combines with basic oxides, such as sodium oxide, potassium oxide, calcium oxide etc.

$$Na_2O + CO_2 \rightarrow Na_2CO_3$$
$$CaO + CO_2 \rightarrow CaCO_3$$

(e) **Photosynthesis** : In the presence of sunlight, plants absorb carbon dioxide. The water present in the plants reacts with carbon dioxide to produce glucose, starch and cellulose. The reaction is catalysed by chlorophyll, the green colouring matter present in plants.

$$6CO_2 + 6H_2O \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + 6O_2$$

$$6nCO_2 + 5nH_2O \rightarrow \underset{\text{Starch or Glucose}}{(C_6H_{12}O_6)_n} + 6nO_2$$

Tests :

(a) A burning splinter of wood is extinguished in it but magnesium ribbon continues to burn in it.

(b) It turns lime water milky.

$$Ca(OH)_2 + \underset{\text{(little)}}{CO_2} \rightarrow \underset{\text{white ppt. (milky)}}{CaCO_3\downarrow + H_2O}$$

$$CaCO_3 + H_2O + \underset{\text{(excess)}}{CO_2} \rightarrow Ca(HCO_3)_2$$

Uses :

(a) It is used for the manufacture of aerated water.

(b) It is used in the refining of sugar.

(c) Dry ice (solid CO_2) is used as refrigerant and in the treatment of local sores.

(d) It is used for providing an inert atmosphere for reactions which cannot be carried out in air.

(e) Carbogen, a mixture of oxygen with about 8 per cent of carbon dioxide, is used for artificial respiration.

(f) It is used as a fire-extinguisher. Since it is heavier than air, it easily displaces oxygen around the fire which is then extinguished for want of oxygen.

Distinction of Carbonates from Bicorbonates

No.	*Tests*	*Carbonates*	*Bicarbonates*
1.	Dry heating	Carbonates of non-alkali-metals and $LiCO_3$ give CO_2.	All bicarbonates give CO_2.
2.	Solubility test	Carbonates of non-alkali-metals do not dissolve in water whereas carbonates of alkali metals dissolve.	All bicarbonates are soluble in water.
3.	Phenolphthalein test	Soluble carbonates give pink colour.	Light pink or no colour is developed.

7.4. Carbon Monoxide

Mol. Formula—CO Mol. Wt.—28

Occurrence :

Carbon monoxide occurs in traces in air, tobacco smoke and volcanic gases. It may also be present in chimney gases and blast furnace gases due to insufficient supply of air.

Methods of Preparations :

(a) When carbon is burnt in an insufficient supply of air or oxygen, carbon monoxide is formed.

$$2C+O_2 \rightarrow 2CO+26{\cdot}42 \text{ Kcal/mole.}$$

(b) It is also obtained by passing carbon dioxide over heated zinc dust or iron filing.

$$Zn+CO_2 \rightarrow ZnO+CO \text{ (Industrial preparation)}$$
$$3Fe+4CO_2 \rightarrow Fe_3O_4+4CO$$

(c) When steam is passed over red hot coke, a mixture of carbon monoxide and hydrogen known as *water gas*, is obtained. It is separated from hydrogen by liquefaction (industrial preparation).

$$C+H_2O \rightarrow CO+H_2$$

(d) Pure carbon monoxide is obtained when potassium ferrocyanide is heated with concentrated sulphuric acid. Dilute sulphuric acid should not be used for this reaction as it liberates extremely poisonous hydrocyanic acid, HCN.

$$\begin{aligned}
K_4[Fe(CN)_6]+3H_2SO_4 &\rightarrow 2K_2SO_4+FeSO_4+6HCN \\
HCN+2H_2O &\rightarrow HCOOH+NH_3 \; [\times 6] \\
2NH_3+H_2SO_4 &\rightarrow (NH_4)_2SO_4 \; [\times 3] \\
HCOOH &\rightarrow CO+H_2O \; [\times 6]
\end{aligned}$$

$$\overline{K_4[Fe(CN)_6]+6H_2SO_4+6H_2O \rightarrow 2K_2SO_4+FeSO_4+3(NH_4)_2SO_4+6CO}$$

Laboratory Preparation :

(a) Carbon monoxide can be prepared in the laboratory by heating crystals of oxalic acid with concentrated sulphuric acid in a round-bottomed flask (Fig. 7.4). A mixture of equal volumes of carbon monoxide and carbon dioxide is evolved and is passed through a wash bottle containing caustic soda solution to absorb carbon dioxide. The issuing carbon monoxide gas is collected over water.

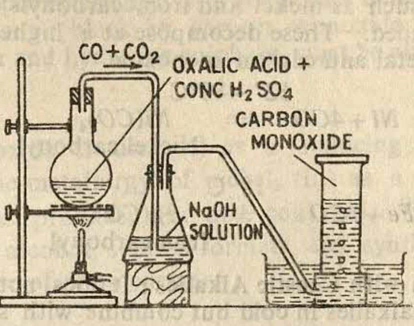


Fig. 7.4

(b) It is conveniently prepared in the laboratory by dehydrating formic acid with concentrated sulphuric acid.

$$HCOOH+H_2SO_4 \rightarrow CO+[H_2O+H_2SO_4]$$

Physical Properties :

(a) Carbon monoxide is a colourless and tasteless gas and has a peculiar faint odour. (b) It is sparingly soluble in water. (c) It is slightly lighter than air (vapour density being 14 as compared to 14.4 of air). (d) It can be liquefied under pressure to a transparent liquid (boiling point – 191·5°C) and can be solidified. (e) It is extremely poisonous.

Chemical Properties :

(a) **Stability** : Carbon monoxide is a stable compound and is not decomposed by heat.

(b) **Combustibility** : It is a combustible gas and burns in air with a blue flame, producing carbon dioxide. It is a non-supporter of combustion.

Formation of Addition Compounds :

(i) **Reaction with Chlorine** : It combines with chlorine in the presence of sunlight or camphor to form carbonyl chloride (phosgene) which is an extremely poisonous gas.

$$CO+Cl_2 \rightarrow COCl_2$$

(ii) **Reaction with Sulphur** : When a mixture of carbon monoxide and vapours of sulphur is passed through a hot tube, carbonyl sulphide is produced.

$$CO+S \rightarrow COS$$

(iii) Reaction with Metals : When it is passed over hot finely divided metals, such as nickel and iron, carbonyls of the respective metals are obtained. These decompose at a higher temperature to give back the metal and carbon monoxide.

$$\underset{}{Ni+4CO} \overset{52°-80°C}{\rightleftharpoons} \underset{\text{Nickel carbonyl}}{Ni(CO)_4}$$

$$Fe+5CO \overset{18°C}{\rightleftharpoons} \underset{\text{Iron carbonyl}}{Fe(CO)_5}$$

(iv) Reaction with Caustic Alkalies : It does not react with solutions of caustic alkalies in cold but combine with solid caustic soda or caustic potash at 200°C under pressure, forming sodium or potassium formate.

$$NaOH+CO \rightarrow \underset{\text{Sodium formate}}{HCOONa}$$

(v) Reaction with Hydrogen : It reacts with hydrogen at 150°C-400°C and a pressure of 200 atmospheres and in the presence of a catalyst (finely divided copper and zinc oxide) to give methyl alcohol.

$$CO+2H_2 \rightarrow \underset{\text{Methyl alcohol}}{CH_3OH}$$

(vi) Reaction with Cuprous chloride : It is absorbed by an ammoniacal solution of cuprous chloride. An addition compound is produced.

$$CuCl+CO+2H_2O \rightarrow \underset{\text{Addition compound}}{CuCl.CO.2H_2O}$$

This reaction is used for removing carbon monoxide from a mixture of gases.

As Reducing Agent : As it is readily oxidised by oxygen, it acts as a powerful reducing agent at high temperatures.

(i) Reaction with Metallic Oxides : Metallic oxides, such as ferric oxide, cupric oxide, etc. when heated in a current of carbon monoxide, are reduced to metals.

$$Fe_2O_3+3CO \rightarrow 2Fe+3CO_2$$
$$CuO+CO \rightarrow Cu+CO_2$$
$$PbO+CO \rightarrow Pb+CO_2$$

(ii) Reaction with Palladium chloride : It reduces a solution of palladium chloride to palladium at the room temperature.

$$CO+H_2O \rightarrow CO_2+H_2$$
$$PdCl_2+H_2 \rightarrow Pd+2HCl$$

Tests :

(a) It burns with a blue flame producing carbon dioxide which turns lime water milky.

(b) It turns an ammoniacal solution of silver nitrate brown.

(c) A filter paper moistened with palladium chloride solution is turned pink, green or black by carbon monoxide. Organic compounds, ammonia and hydrogen sulphide must be absent.

Uses :

Carbon monoxide is used (i) as a reducing agent in metallurgy, (ii) in the metallurgy of nickel, (iii) as a fuel gas in the form of water gas, producer gas and coal gas, (iv) in the manufacture of methyl alcohol, sodium formate and synthetic petrol, (v) in the manufacture of phosgene gas.

7.5. Fuel Gases

Substances which are used as a source of heat energy are known as *fuels*. Amorphous carbon, as charcoal and coke, mineral gas, and many carbon compounds play a very important part in modern life as sources of various kinds of energy. When coal and carboniferous compounds are burnt, heat is evolved which can be employed for heating, preparing food and for many industrial processes. Most of the heat obtained however is converted into other kinds of energy and is used to do mechanical work. Fuels used may be *solids*, *liquids* or *gases*, depending on their physical state. **The gaseous fuels are the best fuels because they possess distinct advantages over solid and liquid fuels. They are smokeless, ashless, easily controlled and economical.** The chief gaseous fuels are :

1. Coal Gas. 2. Producer Gas. 3. Water Gas. 4. Semi-water Gas. 5. Oil Gas. 6. Petrol Gas.

1. Coal Gas : It is a good gaseous fuel as it contains about 95% combustible gases. The calorific value of coal gas is about 450-560 British Thermal Units per cu. ft. The average composition of genuine coal gas is $H_2=38\text{-}55\%$, $CH_4=22\text{-}25\%$, $CO=4\text{-}15\%$, C_2H_4 and $C_2H_2=2{\cdot}5\text{-}5\%$, $N_2=4\%$, some CO_2, O_2 etc.

It is obtained by the distillation of bituminous coal in fire clay retorts at 1000°C in absence of air.

Uses :

(i) As a gaseous fuel and as illuminant.

(ii) In providing inert atmosphere.

(iii) In providing reducing atmosphere in metallurgical preparations.

(iv) In smelting of metals and alloys.

2. **Producer Gas** : It is a cheap industrial fuel but its calorific values is lowest of all gaseous fuels. It is essentially a mixture of carbon monoxide and nitrogen.

$$CO—30\%,\ N_2—60\%;\ CO_2,\ CH_4 \text{ etc.}$$

It is obtained by burning coal in a restricted supply of air.

Uses :

(i) It is mainly used as a gaseous fuel.
(ii) It is also used as a suitable substitute in motor engines.
(iii) In open hearth furnace in the manufacture of steel and glass.

3. **Water Gas** : It is an important gaseous fuel as its calorific value is fairly high (280-310 B. Th. U. per cu. ft.) and its flame is short and hot.

Water gas is essentially mixture of hydrogen and carbon monoxide.

$$H_2—50\%,\ CO—40\%,\ N_2 \text{ and } CO_2.$$

It is obtained by passing steam into a bed of white hot coke.

$$C+H_2O \rightarrow H_2+CO-28 \text{ cal.}$$
$$C+2H_2O \rightarrow 2H_2+CO_2-19 \text{ cal.}$$

Uses :

(i) As a fuel and illuminant, (ii) in the manufacture of hydrogen, (iii) in the manufacture of methyl alcohol.

4. **Semi-water Gas** : Its approximate composition can be given as—

$$CO—27\%,\ H_2—10{\cdot}9\%,\ N_2—56{\cdot}32\%,\ CO_2—4{\cdot}5\%.$$

It is obtained by passing a mixture of steam and air through white hot coke.

Uses :

It is used in the steel industry and for the production of power in internal combustion engines.

5. **Oil Gas** : It is the gaseous fuel used in the laboratories. It is obtained by cracking of kerosene oil. It is a mixture of CH_4, C_2H_6, C_2H_4 etc.

6. **Petrol Gas** : It is a mixture of air and petrol vapours and is obtained by passing air through petrol. Now-a-days we make the use of petrol gas instead of oil gas in laboratories.

7. **Indane Gas** : It is mainly liquid isobutane under pressure. It is used in house-hold as fuel.

7.6. Some Useful Tables

COMPARISON OF THE DIFFERENT ALLOTROPIC FORMS OF CARBON

TABLE—I

Property	Crystalline forms of Carbon		Amorphous forms of Carbon		
	Diamond	*Graphite (Black Lead)*	*Charcaol*	*Lamp Black*	*Gas Carbon*
1. Colour and appearance	Colourless and transparent with brilliant lustre and high refractive index	Grey or black opaque with metallic lustre	Black (opaque), amorphous	Black (opaque), amorphous	Black (opaque) amorphous
2. Hardness and density	Extremely hard, sp. gr. 3·5	Very soft, greasy in touch, marks paper, black, sp. gr. 2·5	Soft and porous. very light, sp. gr. 1·4-1·9	Soft powder, sp. gr. 1·7-1·8	Very hard, sp. gr. 2·35
8. Conductivity (eletctrical)	Bad conductor	Good conductor	Bad conductor	Bad conductor	Bad conductor
4. Effect of heat	When strongly heated, changes to graphite	Stable of high temperature	Changes to graphite	Changes to graphite	Changes to graphite

TABLE—II

COAL

Varieties of Coal	*% of Carbon*
1. Peat	60%
2. Lignite	7%, Burns easily
3. Bituminous	80%
4. Anthracite	90%, Hard, smokeless, high temp., best form of coal

TABLE—III

FUEL GASES

Fuel Gases	*Composition*	*Methods of Preparation*
(i) Water Gas	Mixture of $CO+H_2$	Prepared by passing steam through incandescent coke.
(ii) Semi-water Gas	Mixture of $CO+H_2+N_2$	Prepared by passing a mixture of air and steam over incandescent coke.
(iii) Producer Gas	Mixture of CO_2+N_2	Prepared by burning coke etc. in a limited supply of air.
(lv) Oil Gas	Mixture of gaseous hydrocarbons, CO, H_2 etc.	Prepared by cracking of Kerosene Oil.
(v) Coal Gas	Mixture of H_2, C_2H_2, C_2H_4 etc.	Prepared by destructive distillation of coal.

TYPICAL QUESTIONS WITH ANSWER

1. *What is the difference in the structure of diamond and graphite ?*

Ans. Diamond : C is sp^3-hybridized and there is three-dimensional network making diamond a giant molecule. Diamond is hard and has high boiling point.

Graphite : C is sp^2, one of the p-orbital is used in π-bonding. Due to the π-bonding, graphite has layer structure and layers slip giving softness to graphite. Graphite is a conductor of electricity due to delocalisation of π-electrons.

2. *What do you mean by catenation property ?*

Ans. The property of self linkage is called *catenation* property. $C-C$ bond energy is high and hence 'C' has the greatest catenation property. This property is also found to some extent with silicon, but is absent with *Sn* and *Pb*. As the bond energy of $C-C$, $Si-Si$, $Sn-Sn$, $Pb-Pb$ decreases, catenation property decreases.

3. *CO_2 is a gas but SiO_2 is a solid. Explain.* **(WBJEE 1983)**

Ans. Carbon can form double bonds and so CO_2 is a discrete molecule. Silicon cannot form double bonds, hence SiO_2 forms a giant three-dimensional structure. Thus CO_2 is a gas (low m. pt.) but SiO_2, a high melting solid.

4. *Carbon acts as an abrasive and also as a lubricant. Explain.* **(I. I. T. 1981)**

Ans. Diamond is an allotrope of carbon. This acts as abrasive because the carbon—carbon bonds are very strong and run through the crystals in three dimensions.

In another allotrope, graphite carbon acts as a lubricant. This is because graphite consists of flat, parallel layers in which the carbon atoms form a net work of regular hexagons. These layers are held by weak forces, and even a slight pressure cause them to slide over one another. Hence, graphite is slippery.

5. *CO_2 does not burn in air and does not support combustion but a burning Mg wire continues to burn in it. Explain.*

Ans. The burning *Mg*-ribbon in CO_2 is exothermic and CO_2 dissociates to give O_2 which oxidises *Mg* to *MgO*.

$$2Mg + CO_2 \rightarrow 2MgO + C$$

6. *Diamond is a bad conductor of electricity but graphite is a good conductor. Explain.*

Ans. Diamond has got closed packed structure having sp^3 hybridisation. It has only σ-bond. Graphite has got layer structure and sp^2-hybridisation. It has got π-bond. Therefore, the former is a bad conductor but graphite is a good conductor.

7. *Why CO_2 is not prepared by the action of dil. H_2SO_4 on $CaCO_3$?*

Ans. Dil. H_2SO_4 reacts with $CaCO_3$ to give CO_2.

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 \downarrow + CO_2 + H_2O$$

But insoluble layer of $CaSO_4$ is formed over $CaCO_3$. Hence the reaction ceases. Therefore CO_2 is not prepared by this method.

8. *CO_2 is used as fire-extinguisher. Explain.*

Ans. It is non-supporter of combustion and heavier than air. Hence it breaks the contact of fire with air. Therefore, it extinguishes fire.

QUESTIONS

Long Type Questions :

1. Justify the inclusion of carbon, silicon, tin and lead in the same group of the periodic table.
2. Mention the various gaseous fuels you know and describe their importance. Describe the manufacture of any one of them.
3. Name the different allotropic forms of carbon. Give a short description of the allotropic modifications of carbon and mention their chief uses.
4. How have the crystalline varieties of carbon been obtained artificially? What is the "activated charcoal"? How is it prepared? Mention its important uses.
5. What is the difference between :
   (a) Coal and Coke, (b) Graphite and Diamond, (c) Animal charcoal and Wood charcoal, (d) Lamp black and Gas Carbon ?
6. (a) Describe the principal chemical properties of carbon.
   (b) What happens when :
   (i) a piece of graphite is dipped into hot conc. HNO_3 ?
   (ii) a mixture of CaO and coke is heated at a high temperature ?
   (iii) steam is passed over red hot coke ?
   (iv) pot. ferrocyanide reacts with conc. H_2SO_4 ?
   (v) Mg ribbon is placed in a jar containing CO_2 ?
7. What is producer gas ? How it is obtained ? Mention its uses.
8. (a) How CO_2 is prepared in the laboratory ?
   (b) Why CO_2 is not prepared by the action of dil. H_2SO_4 on $CaCO_3$?
   (c) What happens when CO_2 is passed into Na_2CO_3 solution ?

Short Type Questions :

9. Distinguish between :
   (a) Graphite and Diamond, (b) Producer gas and Water gas.
10. Write notes on :
   (a) Allotropic forms of carbon, (b) Catenation property of IVA elements, (c) Inert pair effect of IVA elements, (d) Water gas, **[BIEC 1983]**
   (e) Producer gas. **[M.U. 1981]**

11. Write down the electronic configuration of carbon orbital wise. Mention the value of different quantum number for the last electron of Carbon.

12. How many elements are placed in IVA sub-group of periodic table ? Name them.

13. Why the elements of IVA sub-group are called p-block elements ?

14. What is the composition of coal gas ?

15. What fuel gas is replaced by petrol gas ?

[**Hint :** Now-a-days petrol gas is used instead of oil gas in laboratories.]

16. (a) What are the chief constituents of producer gas ?

(b) Give three uses of coal gas.

(c) What are the advantages of gaseous fuels over other types of fuels ?

[**Hint :** They are smokeless, ashless, easily controlled and economical.]

17. Explain the following :

(a) CO_2 is a gas but SiO_2 is a solid.

(b) Carbon acts as an abrasive and also as a lubricant. [I. I. T. 1981]

(c) CO_2 does not burn in air but a burning of Mg wire continues to burn it. [I. I. T. 1980]

(d) CO_2 is used in fire extinguisher.

(e) CO_2 is not prepared by the action of dil. H_2SO_4 on $CaCO_3$.

(f) Diamond has a high melting point.

(g) CO_2 is an oxidising agent.

(h) Diamond is less reactive than graphite.

18. Fill up the blank :

(a) CO_2 is————than air. (b) CO is————but CO_2 is————. (c) Diamond is a————conductor but Graphite is a————conductor. (d) Carbon reacts with HNO_3 to give————and————. (e) The number of unpaired electron in carbon in excited state is————. (f) Diamond has got————hybridisation but Graphite has got————hybridisation. (g) Anthracite contains nearly————of carbon, (h) Producer gas is a mixture of————and————. (i) Water gas mainly contains———— and H_2.

19. **Match the Column A with B.**

A	B
(i) CO	(a) Crystalline carbon
(ii) CO_2	(b) Neutral gas
(iii) Diamond	(c) Amorphous carbon
(iv) Peat	(d) Acidic gas

Select and write the correct answer :

20. Mark the wrong statement : Carbon differs from the other elements due to :
    (1) its limitation to a co-ordination number four,
    (2) there are *d*-orbitals in its penceltimate shell,
    (3) its unique ability to form multiple bonds,
    (4) its marked tendency to form long chains (catenation).

21. Mark the oxide which is amphoteric in character :
    (1) CO_2, (2) CO, (3) SnO_2, (4) CaO.

22. What happens when steam is passed over red hot carbon ?
    (1) $C+2H_2O \rightarrow CO_2+2H_2$
    (2) $C+H_2O \rightarrow CO+H_2$
    (3) Water vapour dissociates into H_2 and O_2
    (4) None of the above reaction. [N.C.E.R.T. 1973: C.P.M.T. 1981]

23. The equivalent weight of carbon in CO_2 is :
    (1) 2, (2) 3, (3) 4, (4) 5, (5) 6.

24. Producer gas is a mixture of :
    (1) CO and N_2, (2) CO_2 and H_2.
    (3) CO and H_2, (4) CO_2 and N_2. [C.P.M.T. 1971, 1978]

25. The dry ice is compound of :
    (1) Solid ice without any water, (2) Solid CO_2,
    (3) Solid SO_2, (4) Solid C_6H_6.

26. Diamond and Graphite are :
    (1) Isomers, (2) Allotropes, (3) Isotopes, (4) Polymers.
    [N.C.E.R.T. 1973]

27. Which of the following is a true acid anhydride ?
    (1) Al_2O_3, (2) CO_2, (3) CO, (4) CaO. [N.C.E.R.T. 1976]

28. "Water gas" is an important industrial fuel. It is a mixture of :
    (1) H_2O+air, (2) $CO+H_2$, (3) $CO+CO_2$, (4) H_2O+CO.
    [B.H.U 1979]

29. Which of the following is a good conductor of heat and electricity ?
    (1) Anthracite, (2) Diamond, (3) Charcoal, (4) Graphite.
    [N.C.E.R.T. 1976]

30. Dry powder extinguishers contain :
    (1) sand, (2) sand and Na_2CO_3, (3) sand and baking soda, (4) sand and K_2CO_3. [C.P.M.T. 1980]

31. Lead Pencil contains :
    (1) Pb, (2) Graphite, (3) FeS, (4) PbS. [I.I.T. 1980]

32. Oil gas is obtained in the laboratory by :
    (1) the heating of alcohol,
    (2) the cracking of kerosene oil,
    (3) heating castor oil,
    (4) heating coconut oil. **[C.P.M.T. 1981]**

33. Graphite is used in nuclear reactors :
    (1) as a lubricant, (2) as a fuel,
    (3) for lining the inside of the reactor as an insulator,
    (4) for reducing the velocity of neutrons. **[N.C.E.R.T. 1980]**

□□□

CHAPTER 8

STUDY OF THE NITROGEN GROUP OF ELEMENTS

(Elements of Group V-A)

8.1. Periodic Discussion

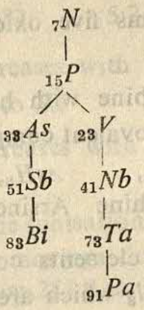
Group V-A of the periodic table contains Nitrogen (*N*), Phosphorus (*P*), Arsenic (*As*), Antimony (*Sb*) and Bismuth (*Bi*). They are *p*-block elements. All have $ns^2\ np^3$ electronic configuration in the outermost orbit. They are generally known as *typical* or *normal elements*. Some of the physical properties of these elements are summarised below :

Element	*Atomic Number*	*Electronic configuration*	*Atomic rodius* (Å)	*First I. P.* (eV.)	*Electrone gativity*	*Density*	*melting point* 0°C	*Boiling point* 0°C
N	7	$[He]\ 2s^2 2p^3$	0·75	14·54	3·0	1·026	—210	—195·8°
P	15	$[Ne]\ 3s^2 3p^3$	1·06	11·0	2·1	1·91 to 2·32	44·1 (white)	280°C
As	33	$[Ar]\ 3d^{10} 4s^2 4p^3$	1·19	10·0	2·0	4·7 5·7	817	610°C sublime
Sb	51	$[Kr]\ 4d^{10} 5s^2 sp^3$	1·38	8·64	1·8	6·68	630·5	1380°
Bi	83	$[Xe]\ 4f^{14} 5d^{10} 6s^2 6p^3$	1·46	8·0	1·7	9·8	271·3	1450°

Thus they have got 5 valence-electrons because all the electrons take part in bond formation.

General Properties of Group VA Elements :

Group V-A of the periodic table contains nitrogen, phosphorus, arsenic, antimony and bismuth while V-B contains vanadium, ninolium, tantalum, and protactinium. The elements of V-A show a marked resemblance as well as a regular gradation in their properties. This justifies their inclusion in the same group of the periodic table.



Similarity :

(i) **Electronic Structure** : All have five (ns^2np^3) electrons in the outermost shell. Out of these 2 are in '*s*' and 3 are in '*p*' orbitals.

$_7N = 2,\ 5\ (2s^2\ 2p^3)$
$_{15}P = 2,\ 8,\ 5\ (3s^2\ 3p^3)$
$_{33}As = 2,\ 8,\ 18,\ 5\ (4s^2\ 4p^3)$
$_{51}Sb = 2,\ 8.\ 18,\ 18,\ 5\ (5s^2\ 5p^3)$
$_{83}Bi = 2,\ 8,\ 18,\ 32,\ 18,\ 5\ (6s^2\ 6p^3)$.

The predominant valency of these elements is therefore 3 and 5.

Mg_3N_2, Ca_3P_2, Na_3As, Zn_3Sb_2, Mg_3Bi_2

Since the shell inner to the outermost in all these elements contains a stable arrangement of 2, 8 or 18 electrons and they are thus all normal elements.

(ii) **Occurrence** : All except nitrogen do not occur in free state.

(iii) **Allotropy** : All except bismuth exists in allotropic form.

Element	*Allotropic forms*
Nitrogen	α-Nitrogen, β-Nitrogen
Phosphorus	White, red, scarlet, black Phosphorus.
Arsenic	Grey, yellow and black Arsenic
Antimony	Metallic, yellow and explosive forms

(iv) **Atomicity** : All are polyatomic.

(v) **Oxidation** state : All show maximum oxidation state +5 with respect to oxygen and minimum oxidation state −3 with respect to hydrogen.

(vi) **Oxides** : All form three oxides (M_2O_3, M_2O_4 and M_2O_5) except nitrogen which forms five oxides (N_2O, NO, N_2O_3, N_2O_4, N_2O_5).

(vii) **Hydrides** : All combine with hydrogen atoms to form hydrides (MH_3) which are covalent compounds.

NH_3,	PH_3,	AsH_3,	SbH_3,	BiH_3
Ammonia	Phosphine	Arsine	Stibene	Bismuthine

(viii) **Chlorides** : All the elements combine with three chlorine atoms to form chlorides MCl_3 which are also covalent compounds. **Nitrogen is unable to form Pentahalides owing to the absence of suitable d-orbitals but subsequent element can do so e. g.**

PCl_5, AsI_5, $SbCl_5$ etc.

P atom..........	$3s$	$3p$	$3d$
Ground state	⇅	↑ ↑ ↑	
Excited state	↑	↑ ↑ ↑	↑

(ix) **Organic compounds** : All of these form trialkyl derivative.

$N(C_2H_5)_3$,	$P(C_2H_5)_3$,	$Bi(C_2H_5)_3$
Triethylamine	Triethylphosphine	Triethyl Bismuthine

Gradation :

(i) **Metallic and electropositive character** : It increases with increase of atomic weight and atomic number. Nitrogen and phosphorus are purely non-metals and Sb and Bi metals. Arsenic (As) may be called metalloid and stands between non-metals and metals.

$$\underbrace{N, P}_{\text{Non-Metals}} \quad \underbrace{As}_{\text{Metalloid}} \quad \underbrace{Sb, Bi}_{\text{Metals}}$$

Like other non-metals nitrogen forms very stable nitrides, phosphorus forms less stable phosphides, arsenic forms unstable arsenides while antimony and bismuth form alloys with other metals. N and P have no lustre while Bi has the best lustre. Like other metals Sb and Bi form cations while N and P behave like typical non-metals in this respect.

(ii) **Density :** It increases with increase of atomic weight from N to Bi.

	N	P	As	Sb	Bi
State :	gas	solid	solid	solid	solid
Density :	0·96	1·82	5·7	6·6	9·8

(iii) **Boiling Point :** It increases with increase of atomic weight and atomic number from N to Bi.

(iv) **Melting Point :** It increases with increase of atomic weight from N to P.

(v) **Ionisation Energy :** The ionisation energy of nitrogen is very high (336 Kcal/mole). On moving downward in the group the value gradually decreases from 253·9 to 148·9 Kcal/mole.

(vi) **Oxides :** Acidic character decreases as the atomic weight increases.

N_2O_3	P_2O_3	As_2O_3	Sb_2O_3	Bi_2O_3
Acidic	Weakly acidic	Amphoteric	Amphoteric	Basic

Action of Water and Alkalies on Oxides :

$(M = N, P, As, Sb, Bi)$

Oxides	*Action of Water*	*Action of Alkalies*
Trioxides	$N_2O_3+H_2O \rightarrow 2HNO_2$ $P_2O_3+H_2O \rightarrow 2H_3PO$	$As_2O_3+6NaOH \rightarrow 2Na_3AsO_3+3H_2O$ Sod. arsenite
Tetraoxides	$N_2O_4+H_2O \rightarrow HNO_2+HNO_3$ $P_2O_4+H_2O \rightarrow H_3PO_3+H_3PO_4$	Sb_2O_4 forms hypo-antimonites on fusing with alkalies
Pentaoxides	$N_2O_5+H_2O \rightarrow 2HNO_3$ $P_2O_5+8H_2O \rightarrow 2H_3PO_4$ $As_2O_5+3H_2O \rightarrow 2H_3AsO_4$	$Bi_2O_5+6NaOH \rightarrow 2Na_3BiO_4+3H_3O$

(vi) **Oxyacids :** They show regular gradation in their strength.

HNO_3,	H_3PO_4,	H_3AsO_4,	H_3SbO_4
strong	strong	weak	very weak

(viii) **Hydrides** :They show regular gradation in their properties.

Terms	*Nature*
Stability	Decreases from NH_3 to BiH_3
Poisonous nature	Increases from NH_3 to SbH_3. NH_3 is non-poisonous but AsH_3 and SbH_3 are poisonous
Basic nature	Decreases from NH_3 to BiH_3, NH_3 (Basic), PH_3 (very weak base), AsH_3, SbH_3, and BiH_3 (Neutral)
Reducing character	Increases with increase of mol. wt. NH_3 is a mild reducing agent but BiH_3 is the strongest.

(ix) Chlorides :

(a) *Trichlorides* : All form trichlorides which are hydrolysed by water. Their reactivity towards water decreases with rise in molecular weight.

$$NCl_3+3H_2O \rightarrow NH_3+3HClO$$
$$PCl_3+3H_2O \rightarrow H_3PO_3+3HCl$$
$$AsCl_3+3H_2O \rightarrow H_3AsO_3+3HCl$$
$$SbCl_3+H_2O \rightarrow SbOCl+2HCl$$
$$BiCl_3+H_2O \rightarrow BiOCl+2HCl$$

The boiling points of trichlorides also gradually increases from NCl_3 to $BiCl_3$.

(b) *Pentachloride* : Only PCl_5 and $SbCl_5$ are the stable pentachlorides known which dissociate on heating and are hydrolysed by water.

$$PCl_5+4H_2O \rightarrow H_3PO_4+5HCl$$
$$SbCl_5+4H_2O \rightarrow \underset{\text{Antimonic acid}}{H_3SbO_4}+5HCl$$

Nitrogen Differs from P, As, Sb and Bi :

(i) Nitrogen has got no *d*-orbitals in valency shell, hence formation of NCl_5 is not possible and cannot form complexes.

(ii) It is a diatomic gas.

(iii) The size of the atom is small, but the value of electronegativity is high. Hence it is non-metallic.

(iv) It has various oxidation states.

O. S.	−3	−2	−1	−1/3	+1	+2	+3	+4	+5
Compds	NH_3	NH_2NH_2	NH_2OH	N_3H	N_2O	NO	N_2O_3	NO_2	N_2O_5
Nature	Basic	Basic	Basic	Acidic	Neutral	Neutral	Acidic	Acidic	Acidic

8.2. Nitrogen (N).

Atomic Number : 7 Atomic Mass = 14

Electronic configuration : $1s^3\ 2s^2\ 2p_x^1\ p_y^1\ p_z^1$

Occurrence : Nitrogen is the main constituent of air. Air contains about 78% Nitrogen by volume. All natural water contains nitrogen in the dissolved state. In the combined state, it occurs as nitre (or saltpetre) KNO_3 and as chile saltpetre, $NaNO_3$. Nitrogen is an essential constituent of all proteins and is, therefore, present in all animal and plant tissues.

Methods of Preparation :

Laboratory Method : Nitrogen is prepared by heating ammonium nitrite solution. In actual practice, it is prepared in the laboratory by warming a mixture of 1 part of ammonium chloride, 1 part of sodium nitrite and 5 parts of water in a round-bottomed flask provided with a thistle funnel and delivery tube.

$$NH_4Cl + NaNO_2 \rightarrow NH_4NO_2 + NaCl$$
$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

Nitrogen evolved is bubbled through a solution of potassium dichromate acidified with sulphuric acid to remove ammonia and oxides of nitrogen (Fig. 8.1). It is collected over water.

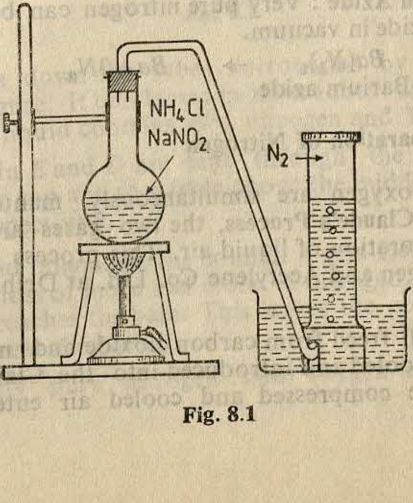


Fig. 8.1

Other Methods :

1. From Ammonium Dichromate : It may be prepared by heating ammonium dichromate gently.

$$(NH_4)_2\,Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O$$

The reaction is vigorous. Nitrogen is evolved and a green residue of chromic oxide is left behind.

2. From Ammonia :

(a) It is prepared by passing ammonia over red hot cupric oxide.

$$2NH_3 + 3CuO \rightarrow N_2 + 3H_2O + 3Cu$$

(b) Ammonia can also be oxidised to nitrogen by passing chlorine gas through its strong solution.

$$8NH_3 + 3Cl_2 \rightarrow N_2 + 6NH_4Cl$$

(c) Nitrogen can also be prepared by warming a paste of bleaching powder with a strong solution of ammonia.

$$Ca(OCl)Cl \rightarrow CaCl_2 + O\ [\times 3]$$
$$2NH_3 + 3\text{'}O\text{'} \rightarrow N_2 + 3H_2O$$
$$\overline{3Ca(OCl)Cl + 2NH_3 \rightarrow 3CaCl_2 + N_2 + 3H_2O}$$

3. From Air : The two major constituents of air are nitrogen and oxygen; Nitrogen can be isolated from air by removing oxygen by

(i) Burning phosphorus :

$$P_4 + 5O_2 \rightarrow 2P_2O_5$$
$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$$

(ii) Fractional Evaporation of Liquid Air : Nitrogen is prepared on an industrial scale by fractional evaporation of liquid air. The boiling point of oxygen (−183°C) is higher than that of nitrogen (−196°C). Hence, nitrogen evaporates first leaving behind liquid oxygen.

4. From Barium Azide : Very pure nitrogen can be prepared by heating barium azide in vacuum.

$$\underset{\text{Barium azide}}{Ba(N_3)_2} \rightarrow Ba + 3N_2$$

Industrial Preparation of Nitrogen :

Nitrogen and oxygen are simultaneously manufactured from liquid air. In the **Claude's Process**, the two gases are obtained by the fractional evaporation of liquid air. This process is being used by the Indian Oxygen and Acetylene Co. Ltd. at Delhi, Kanpur and Calcutta.

Air is first of all freed from carbon dioxide and moisture. It is then compressed, cooled and introduced into the Claude's plant at *A* (Fig. 8.2). The compressed and cooled air enters the pipes which are surrounded by liquid oxygen. As the air passes through the pipes, some of it gets condensed and falls in the space *D*. The liquid that collects in *D* contains 50% of oxygen and 50% of nitrogen. The uncondensed air collects in empty space at the

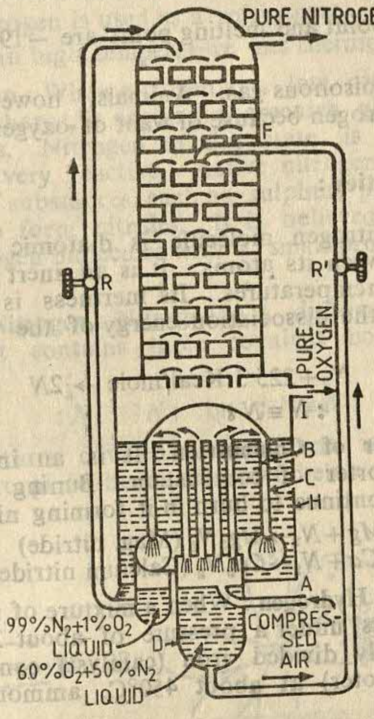


Fig. 8.2

top and passes down the tubes surrounded by liquid oxygen as shown in the figure. It condenses in these tubes and collects at *E*. The condensed liquid contains 99% nitrogen and 1% oxygen.

The liquid in *E* and *D* are sent through the regulating valves *R* and *R'* to the top and to a little above the middle of the fractionating column respectively.

As the liquid falls down the column it gets richer and richer in oxygen due to loss of more and more of nitrogen. It is 98% oxygen by the time it reaches the base. This leaves the column through the exit provided near the base.

Thus, nearly pure nitrogen nnd oxygen are simultaneously prepared.

Physical Properties :

(a) Nitrogen is a colourless, odourless and tasteless gas.

(b) It is only slightly lighter than air. ($D_{air} = 14{\cdot}4 = D_{N_2} = 14$);

(c) It is very slightly soluble in water. Its solubility is even less than that of oxygen.

(d) Its boiling point and melting point are $-196°C$ and $-210°C$ respectively.

(e) It is not a poisonous gas. Animals, however, die in an atomosphere of nitrogen because of want of oxygen.

Chemical Properties :

(a) **Stability** : Nitrogen molecule is diatomic and has a triple covalent bond between its atoms. It is an inert element, particularly at ordinary temperatures. Its inertness is in accord with the high value for the dissociation energy of the molecule (225·3 Kcal/mole).

$$N_2 + 225{\cdot}3 \text{ Kcal/mole} \rightarrow 2N$$

$$:N\equiv N:$$

(b) **Non-supporter of Combustion** : It is an incombustible gas and is a non-supporter of combustion. Buning magnesium and calcium, however, continue to burn in it forming nitrides.

$$3Mg + N_2 \rightarrow Mg_3N_2 \text{ (Mag. nitride)}$$

$$3Ca + N_2 \rightarrow Ca_3N_2 \text{ (Calcium nitride)}$$

(c) **Reaction with Hydrogen** : When a mixture of nitrogen (1 part) and hydrogen (3 parts) under a pressure of about 200 atomsphere is passed over finely divided iron (catalyst) containing a little molybdenum (Promoter) at about 450°C, ammonia is produced (Haber's process).

$$\underset{1\text{ wt.}}{N_2} + \underset{3\text{ wt.}}{3H_2} \rightleftharpoons 2NH_3 + 24{\cdot}08 \text{ Kcal}$$

(d) **Reaction with Oxygen** : When air is passed through an electric arc at 3000°C, then "NO" is obtained.

$$N_2 + O_2 \rightleftharpoons 2NO - 43{\cdot}2 \text{ Kcal}$$

(e) **Reaction with Calcium carbide** : When nitrogen is passed over heated calcium carbide at 1000°C, calcium cyanamide is produced.

$$\underset{\text{Cal. Carbide}}{CaC_2} + N_2 \rightarrow \underset{\text{Cal. Cyanamide}}{CaNCN} + C$$

(f) **Reaction with Alumina** : When nitrogen is passed over a mixture of alumina and coke at 900°C, aluminium nitride is produced.

$$Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO$$

Uses :

(a) It is used for the manufacture of ammonia, nitric acid, calcium cyanamide and nitrides.

(b) It is used for providing an inert atmosphere in certain metallurgical operation and in electric bulbs.

(c) Liquid nitrogen is used as a refrigerant.

(d) It is used in high temperature gas thermometers.

Active Nitrogen : When nitrogen at a low pressure is subjected to an electric discharge, it acquires a greenish glow which persists for several hours. Nitrogen in this state is known as *active nitrogen* and is very reactive. Active nitrogen readily combines with a number of substances, such as sulphur, phosphorus, tin and alkali metals, to form nitrides. It is believed to consist mostly of activated nitrogen molecules with a small proportion of atomic nitrogen.

Structure of Nitrogen : Nitrogen is a diatomic molecule and it is non-polar. It contains three covalent bonds between two nitrogen atoms.

$$:N\vdots\ \vdots N: \quad \text{or} \quad :N\equiv N:$$

Among the three covalent bonds, one is a sigma (σ)-bond and other two are pi (π)-bonds as shown below.

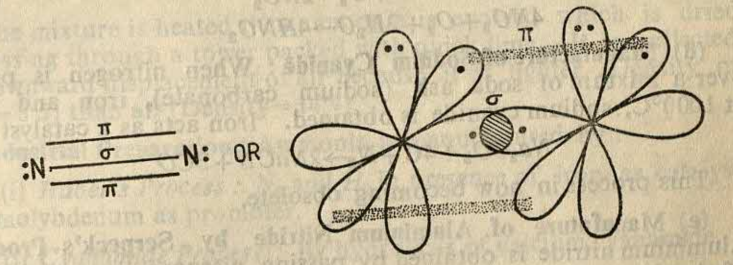


Fig 8.4

Test : (i) It is a colourless gas. It extinguishes burning lighted tappers.

(ii) It is not absorbed by red hot copper. (Difference from oxygen)

(iii) It does not turn lime water milky. (Difference from CO_2)

(iv) It is absorbed by heated magnesium. The product gives NH_3 on treatment with water.

$$3Mg+N_2 \rightarrow Mg_3N_2$$
$$Mg_3N_2+6H_2O \rightarrow 3Mg(OH)_2+2NH_3$$

Fixation of Nitrogen : The conversion of atmospheric nitrogen into compounds of nitrogen either by natural or artificial means is known as fixation of nitrogen. Important methods for the artificial fixation of nitrogen are described below :

(a) **Haber's process for the Manufacture of Ammonia** : When a mixture of 1 part of nitrogen and 3 parts of hydrogen under a pressure of 200 atmosphere is passed over finely divided iron (catalyst) containing a little molybdenum (promoter) at about 450°C, ammonia is produced.

$$N_2+3H_2\rightleftharpoons 2NH_3$$

(b) **Manufacture of Calcium Cyanamide** : When nitrogen is passed over heated calcium carbide at about 1000°C calcium cyanamide is produced. The most important use of calcium cyanamide is for production of nitrogenous fertilizers.

$$CaC_2+N_2\rightarrow CaNCN+C$$

(c) **Manufacture of Nitric Acid by Birkland and Eyde's Process** : Air is blown through an electric arc when nitrogen combines with oxygen to produce nitric oxide. On cooling, it gets oxidised to nitrogen peroxide by oxygen present along with it. This is converted into nitric acid when dissolved in water in the presence of air.

$$N_2+O_2\rightleftharpoons 2NO$$
$$2NO+O_2\rightarrow 2NO_2$$
$$4NO_2+O_2+2H_2O\rightarrow 4HNO_3$$

(d) **Manufacture of Sodium Cyanide** : When nitrogen is passed over a mixture of soda ash (sodium carbonate), iron and coke at 1000°C, sodium cyanide is obtained. Iron acts as a catalyst.

$$Na_2CO_3+4C+N_2\rightarrow 2NaCN+3CO$$

This process in now becoming obsolete.

(e) **Manufature of Aluminium Nitride by Serpeck's Process** : Aluminium nitride is obtained by passing nitrogen over a mixture of alumina and coke at 900°C. This method also has now become outdated.

$$Al_2O_3+3C+N_2\rightarrow 2AlN+3CO$$

AMMONIA

Molecular Formula : NH_3 Mol. wt. = 17

Occurrence :

Ammonia is present only in traces in the air and in natural water. It is being formed by the decomposition of nitrogeneous organic matter.

Laboratory Preparation :

Principle : Ammonia is prepared in the laboratory by heating ammonium chloride (NH_4Cl) and slaked lime (3 parts) in a flask.

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + 2H_2O$$

Description . The mixture of NH_4Cl and $Ca(OH)_2$ is taken in a flask as shown in fig 8.5.

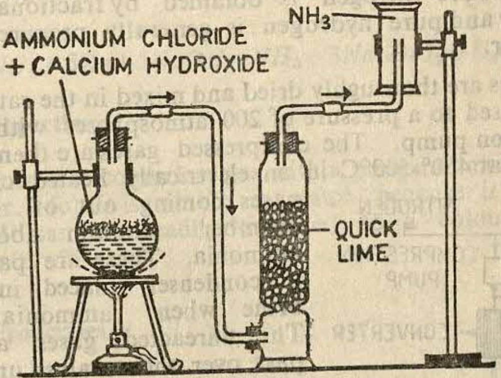


Fig. 8.5

The mixture is heated then ammonia is evolved which is dried by passing through a tower packed with quick lime. It is collected by downward displacement of air because it is lighter (Density of $NH_3 = 8{\cdot}5$) than air (Density = 14·4).

Industrial Preparation : Ammonia is manufactured by :

(i) *Haber's Process :* N_2 and H_2 in presence of iron as catalyst and molybdenum as promoter.

(ii) *Cyanamide Process :* By hydrolysis of calcium cyanamide.

(iii) *Serpeck's Process :* By the action of bauxite, coke and nitrogen.

(i) **Haber's Process** : *Principle :* Nitrogen and hydrogen combines under suitable conditions to form ammonia.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 24{\cdot}08 \text{ K cal.}$$

This reaction is reversible, exothermic and is accompanied by a decrease in volume. The most favourable conditions for the formation of ammonia are described below :

(i) *Temperature :* According to Le-Chatelier's Principle, a low temperature will favour the forward reaction. The optimum temperature for this reaction has been experimentally found to be 450°C-500°C.

(ii) *Pressure :* According to Le-Chatelier's Principle, a high pressure will favour the forward reaction. The suitable pressure is 200 atmosphere.

(iii) *Catalyst :* Finely divided iron containing a little molybdenum (Promoter) is used as a catalyst to increase the velocity of the reaction.

(iv) *Purity of Gases :* Nitrogen and hydrogen used must be pure. Impurities, if present, will poison the catalyst.

Process : Pure nitrogen is obtained by fractional evaporation of liquid air and pure hydrogen is generally prepared by electrolysis of water.

The gases are thoroughly dried and mixed in the ratio of 1 : 3 and are compressed to a pressure of 200 atmospheres with the help of a compression pump. The compressed gases are then passed over the catalyst at 450°-500°C in an electrically heated chamber. The gases coming out of the catalyst chamber contain about 10-20% ammonia. These are passed through a condenser placed in refrigerated brine when ammonia condenses. The unreacted gases are made to pass over the catalyst under pressure with the help of an air circulation pump (Fig. 8.6). Thus, the whole process is continuous. This is the cheapest method available for the industrial preparation of ammonia. This is the modern process.

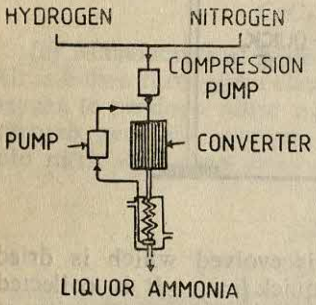


Fig. 8.6

(ii) Cyanamide process : When atmospheric N_2 is passed over calcium carbide heated to 1000°C, calcium cyanamide is formed. This when decomposed with steam, evolves NH_3 gas.

$$CaC_2 + N_2 \rightarrow CaCN_2 + C$$
$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3$$

(iii) Serpeck's Process : NH_3 is obtained as a by-product in the purification of alumina from bauxite. When air is passed over a mixture of alumina and coke heated to 1800°C, aluminium nitride is formed. This on hydrolysis with steam yields ammonia.

$$Al_2O_3 + 3C \rightarrow 2AlN + 3CO$$
$$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3$$

The cyanamide and Serpeck's process are *obsolete* these days.

Other Methods of Preparation :

(i) By heating Microcosmic salt : When microcosmic salt is heated alone then ammonia is obtained.

$$NaNH_4HPO_4 \rightarrow NaPO_3 + NH_3 + H_2O$$

(ii) By boiling metal nitride with H_2O :

$$Mg_3N_2+6H_2O\rightarrow 3Mg(OH)_2+2NH_3$$
$$AlN+3H_2O\rightarrow Al(OH)_3+NH_3$$

(iii) By boiling a mixture of metal nitrate or nitrite with zinc and sodium hydroxide.

$$Zn+2NaOH\rightarrow Na_2ZnO_2+2\text{'}H\text{'}\ [\times 4]$$
$$\underline{NaNO_3+8\text{'}H\text{'}\rightarrow NH_3+NaOH+2H_2O}$$
$$NaNO_3+4Zn+7NaOH\rightarrow NH_3+4Na_2ZnO_2+2H_2O$$

Similarly

$$NaNO_2+3Zn+5NaOH\rightarrow NH_3+3Na_2ZnO_2+H_2O.$$

Physical Properties :

(a) Ammonia is a colourless gas with a pungent smell. (b) It is lighter than air. (c) It is soluble in water because it is a polar covalent. (d) It can be readily liquefied to a colourless liquid which boils at 33·4°C.

Chemical Properties :

Ammonia

- Stability
- Basic properties
- Oxidation of NH_3
- Reaction with alkali metals
- Precipitation of metal hydroxides
- Formation of complex compounds

(A) Stability : It is extremely unstable because its formation from elements is accompanied by the evolution of only 11·04 Kcal/mole.

$$2NH_3 \overset{500°C}{\rightleftharpoons} N_2+3H_2$$

(B) Basic Properties : The solution of ammonia gas possess basic properties, because (a) it turns red litmus blue and tumeric paper brown, (b) it reacts with acids to form salts.

$$NH_3+HCl\rightarrow NH_4Cl$$
$$2NH_3+H_2SO_4\rightarrow(NH_4)_2SO_4$$

NH_4OH is a weak base because it dissociates incompletely.

$$NH_4OH\rightleftharpoons NH_4^{+}+OH^{-}\ (K=1{\cdot}8\times 10^{-5})$$

(C) Oxidation of Ammonia or **NH_3 is a reducing Agent** : It acts as a reducing agent because it gives N_2 or NO with oxidising agent. In the following reactions ammonia is oxidised to N_2 or NO.

(i) *Reaction with Oxygen :*

$$4NH_3+3O_2\rightarrow 2N_2+6H_2O$$

(ii) *Reaction with red hot Copper oxide :* When ammonia is passed over red hot CuO then N_2 is obtained.

$$2NH_3+3CuO \rightarrow 3Cu+N_2+3H_2O$$

(iii) *Reaction with air in presence of catalyst :*

$$4NH_3+5O_2 \xrightarrow[\text{asbestos } 700^\circ C]{\text{Platinised}} \underset{\text{Nitric oxide}}{4NO} + 6H_2O$$

(D) Reaction with Alkali Metals : When ammonia is passed over heated sodium or potassium, amides are produced.

$$2Na+2NH_3 \rightarrow \underset{\text{Sodamide}}{2NaNH_2} + H_2$$

(E) Precipitation of Metal Hydroxides : It precipitates the hydroxides of heavy metals from the solution of their salts.

(i) *Reaction with Ferric chloride :* It gives a reddish brown precipitate of Ferric Hydroxide with a Ferric salt solution.

$$FeCl_3+3NH_4OH \rightarrow Fe(OH)_3\downarrow +3NH_4Cl$$

(ii) *Reaction with Chromium salt* : It gives green precipitate of chromium hydroxide.

$$Cr_2(SO_4)+6NH_4OH \rightarrow 2Cr(OH)_3\downarrow +(NH_4)_2SO_4$$

(iii) *Reaction with Aluminium salt :* It gives white gelatinous precipitate of aluminium hydroxide.

$$Al_2(SO_4)_3+6NH_4OH \rightarrow 2Al(OH)_3\downarrow +3(NH_4)_2SO_4$$

(F) As Complexing Agent : Ammonia forms complex compounds with the following salts.

(i) *Reaction with Copper sulphate :* It reacts with little NH_4OH to give bluish white precipitate of $Cu(OH)_2$.

$$\underset{\text{Solution}}{CuSO_4}+2NH_4OH \rightarrow \underset{\text{Bluish white}}{Cu(OH)_2\downarrow} +(NH_4)_2SO_4$$

Copper sulphate solution reacts with excess of NH_4OH solution to give deep blue solution of [tetrammine Cu (II) sulfate]

$$CuSO_4+4NH_4OH \rightarrow [Cu(NH_3)_4]SO_4+4H_2O$$

(ii) *Reaction with Silver chloride :* It reacts with silver chloride to give soluble diammine Ag (I) chloride, $[Ag(NH_3)_2]Cl$

$$AgCl+2NH_4OH \rightarrow [Ag(NH_3)_2]Cl+2H_2O$$

(iii) *Reaction with Zinc sluphate* :

(a) $\underset{\text{Sol}^n}{ZnSO_4}+\underset{\text{little}}{2NH_4OH(\text{Soln.})} \rightarrow \underset{\text{White ppt}}{Zn(OH)_2\downarrow} +(NH_4)_2SO_4$

(b) $\underset{\text{Soln.}}{ZnSO_4}+\underset{\text{Excess}}{4NH_4OH(\text{Soln.})} \rightarrow \underset{\text{Soln.}}{[Zn(NH_3)_4]SO_4}+4H_2O$

Other Reactions :

(G) Reaction with Halogens :

(i) Excess NH_3 and little Cl_2 : When NH_3 reacts with little chlorine then N_2 is obtained.

$$8NH_3+3Cl_2 \rightarrow N_2+6NH_4Cl$$

(ii) Little NH_3 and Excess of Cl_2 : It gives nitrogen trichloride which is an explosive.

$$NH_3+3Cl_2 \rightarrow NCl_3+3HCl$$

(iii) Reaction with Br_2 :

$$8NH_3+3Br_2 \rightarrow N_2+6NH_4Br$$

(iv) Reaction with Iodine : Liquid ammonia reacts with iodine to form nitrogen triodide which behaves as an explosive in the dry state.

$$2NH_3+3I_2 \rightarrow \underset{\text{Nitrogen triodide}}{NI_3.NH_3} + 3HI$$

(H) Reaction with CO_2 : It forms urea which is an important fertiliser.

$$2NH_3+CO_2 \rightarrow \underset{\text{Urea}}{NH_2CONH_2}+H_2O$$

(I) Reaction with Mercurous Chloride or Nitrate : It gives black precipitate with mercurous chloride or nitrate due to mercury amido-chloride.

$$Hg_2Cl_2+2NH_4OH \rightarrow \underbrace{Hg + Hg(NH_2)Cl}_{\text{Mercury amido chloride}} + NH_4Cl+2H_2O$$

Uses : Ammonia is used

(a) in the manufacture of HNO_3 by Ostwald process,

(b) in the manufacture of fertiliser such as ammonium sulphate, ammonium phosphate etc.,

(c) in the manufacture of rayon,

(d) as cleansing agent for the removal of grease and oils.

(e) Liquefied ammonia is used as refrigerant in ice making and in cold storages. This is due to the ease with which it can be liquefied at low pressure and its high heat of vaporisation.

SUMMARY CHART

Preparation :

(1) By heating any amm. salt with alkali $\rightarrow NH_3 + \text{salt} + H_2O$

(2) By heating Microcosmic salt. $NaNH_4HPO_4 \rightarrow NH_3 + NaPO_3 + H_2O$

(3) By the action of water on metal nitrides. $AlN + H_2O \rightarrow Al(OH)_3 + NH_3$

(4) By boiling nitrate or nitrites with Zn and $NaOH$ $4Zn + NaNO_3 + 7NaOH \rightarrow 4Na_2ZnO_2 + NH_3 + 2H_2O$

(5) Haber's Process

$$N_2 + 3H_2 \underset{Mo\ \text{(Promoter)}}{\overset{Fe\ \text{(Catalyst)}}{—}} 2NH_3 + 46\ \text{KJ}$$

(6) Cyanamide Process $CaCN_2 + 3H_2O \rightarrow CaCO_3 \times 2NH_3$

(7) Serpeck's Process $AlN + H_2O \rightarrow NH_3 + Al(OH)_3$

NH_3 Mol. wt. 17

sp^3 Tetra-hedral; Pyramidal shape, Polar covalent, Hydrogen bond, Soluble in water, dried by quick lime, turns nesslebbbb relagent brown.

$\xrightarrow{H_2O} NH_4^+ + OH^- = NH_4OH$ (Molecule)

$\xrightarrow{Cl_2}$ Excess $NCl_3 + HCl$; Little $N_2 + NH_4Cl$

$\xrightarrow{HX} NH_4X$

$\xrightarrow{O_2} NO + H_2O$

$\xrightarrow[\text{metals}]{\text{Alkali}} NaNH_2 + H_2$

$\xrightarrow[\text{sol}^n]{Fe^{+++}\text{ion}} Fe(OH)_3$

$\xrightarrow[\text{Sol}^n]{CuSO_4}$ Little NH_3 $Cu(OH)_2 + (NH_4)_2SO_4$; Excess NH_3 $[Cu(NH_3)_4]SO_4$ Deep Blue soln $+ (NH_4)_2SO_4$

$\xrightarrow{CO_2} NH_2CONH_2$ (Urea)

$\xrightarrow{AgCl} [Ag(NH_3)_2]Cl + NH_4Cl$

$$\xrightarrow{Hg_2Cl_2} \underbrace{Hg + Hg(NH_2)Cl}_{\text{Black}} + NH_4Cl$$

Desiccation : By quick lime, CaO or soda lime or solid $NaOH$, KOH soda lime.

Uses : (i) As Fertiliser, (ii) As Refrigerant, (iii) In the manufacture of HNO_3.

Tests : (i) It turns red-litmus blue.

(ii) It turns moist mercurous nitrate paper black.

(iii) It gives white fumes with HCl due to formation of NH_4Cl.

(iv) It turns Nessler's Reagent $K_2[HgI_4]$ brown. It is the delicate test for ammonium salts.

Nessler's Reagent : When KI solution is added to mercuric chloride solution then red precipitate of HgI_2 is obtained. It is soluble in excess of Potassium iodide solution, giving colourless solution of $K_2[HgI_4]$. Now excess of KOH solution is added to the solution which is called Nessler's Reagent.

$$HgCl_2 + 2KI \rightarrow HgI_2 + 2KCl$$

$$HgI_2 + 2KI \rightarrow K_2[HgI_4]$$

Structure of ammonia : The electronic structure of ammonia is shown in the chapter electronic theory of valency.

In ammonia, nitrogen is highly electronegative. Hence nitrogen in ammonia forms weak electrostatic force with hydrogen. Hence it contains hydrogen bond. In ammonia, nitrogen molecule is sp^3 hybridised. Its structure is tetrahedral but shape is pyramidal.

To find out hybridisation of NH_3 : See valency chapter.

To prove that ammonia contains nitrogen and hydrogen :

(i) *Hydrogen* : When ammonia is passed over heated sodium then sodium amide is obtained and the gas is collected over water. Its property is tested. It is colourless, odourless and it burns with blue flame. It is adsorbed by heated palladium. Hence the gas is Hydrogen. Therefore ammonia contains hydrogen.

$$2Na + 2NH_3 \rightarrow 2NaNH_2 + H_2$$

(ii) *Nitrogen* : When ammonia is passed over red hot CuO then a gas is obtained. This is collected over water. It is an inactive gas and it is absorbed by heated Mg. Hence the gas is Nitrogen. Therefore, ammonia contains Nitrogen.

$$3CuO + 3NH_3 \rightarrow N_2 + 3H_2O + 3Cu$$

8.4. Nitric Acid

Molecular Formula—HNO_3 Molecular Weight—63

Occurence : It occurs in free state in little amount in rain water. It occurs in combined state as nitrates.

Laboratory Preparation :

Nitric acid is prepared in the laboratory by heating sodium nitrate (Chile salt petre) with conc. H_2SO_4 in a glass retort. This reaction is possible because HNO_3 is more volatile than conc. H_2SO_4 (high B. P.) Vapours of nitric acid are condensed in a receiver cooled under water (Fig 8.7).

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$

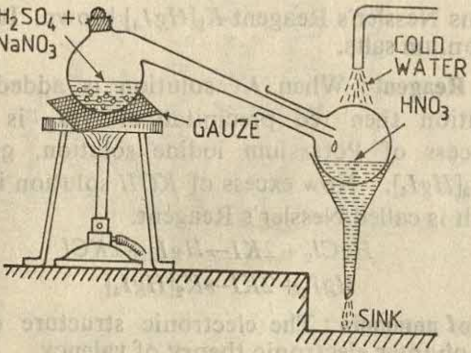


Fig. 8.7

The acid thus obtained is yellow in colour due to the presence of nitrogen dioxide in it. A small quantity of water is also present in it and is removed in its re-distillation with concentrated sulphuric acid. Nitrogen dioxide is removed by passing a current of hot dry air or carbon dioxide through it.

Manufacture of Nitric Acid : It is manufactured by (a) Chile salt petre process, (b) Birkland Eyde process, (c) Ostwald process.

(A) **Chile salt petre (Old Retort Process)** : The principle is the same as laboratory process.

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$

(B) **Birkland and Eyde's Process (Arc Process) (From air)** : *Principle* : This method is based on the following reactions.

(i) $N_2 + O_2 \overset{3000°C}{\rightleftharpoons} 2NO - 43{\cdot}2$ K. cal. (Electric Arc)

(ii) $2NO + O_2 \xrightarrow{50°C} 2NO_2$ (Oxidation chamber)

(iii) $2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$ (Absorption tower).

HNO_2 is separated from HNO_3 by fractional distillation and heated then NO is obtained. It is sent to oxidation chamber and the process is repeated.

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O.$$

Reaction No (i) is reversible and is accompanied by absorption of heat. According to Le Chatelier's Principle, a high temperature will favour the forward reaction. The reaction is, therefore, carried out at about 3000°C and the pressure will have no effect on the reaction.

Process : (i) Electric Arc : Air free from carbon dioxide and moisture is blown through an electric Arc struck between two water-cooled copper electrodes. The Arc is spread in the form of a disc by means of a powerful electromagnet placed at right angles, to the electrodes. As the air passes through the electric Arc, it gets heated to about 3000°C and some nitric oxide is produced.

$$N_2+O_2 \rightleftharpoons 2NO-43{\cdot}2 \text{ K cal.}$$

There is no effect of pressure on this reaction.

(ii) **Cooler** : The air is forced rapidly across the Arc so that the resulting gas mixture is cooled as rapidly as possible. This is necessary to avoid the decomposition of nitric oxide produced and to enable it to get oxidised to nitrogen dioxide.

(iii) **Boiler** : The gases leaving the electric Arc chamber contains about 50% of nitric oxide and are at a temperature of about 1000°C. The gases are passed through boilers which produce the steam for various operations. The gases leave the boiler at about 150°C.

(iv) **Oxidation chamber** : The gases from the boiler are led into an oxidation chamber where nitric oxide combines with oxygen to form nitrogen peroxide.

$$2NO+O_2 \rightarrow 2NO_2.$$

(v) **Absorption Tower** : The gases are next passed into an absorption tower packed with quartz. Water or dilute nitric acid is continously sprayed in this tower from the top. Nitrogen peroxide combines with water in the presence of oxygen to produce nitric acid.

$$2NO_2+H_2O+\tfrac{1}{2}O_2 \rightarrow 2HNO_3.$$

The acid thus produced collects at the base of the tower and contains about 50 per cent nitric acid (Fig. 8.8). The unreacted

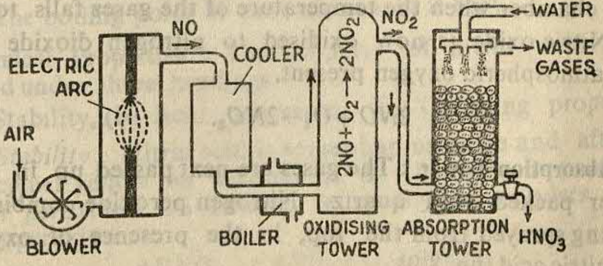


Fig. 8.8

gases are again blown through the electric Arc chamber and the process is repeated.

Defect : This method has been totally given up due to high power requirements and great wear and tear of the plants.

Ostwald's Process :

This is most important and by far the best method for the manufacture of nitric acid. It is based on the catalytic oxidation of ammonia by atmospheric oxygen when nitric acid is formed.

Principle : Amonia, produced by Haber's process, is mixed with air (1 : 7) and passed over platinum gauze at 800°C. It gets oxidised to nitric oxide which combines with oxygen to produce nitrogen peroxide. Nitrogen peroxide combines with water in the presence of oxygen to produce nitric acid.

$$4NH_3+5O_2\rightarrow 4NO+6H_2O+215\text{ Kcal.}$$

$$2NO+O_2\rightarrow 2NO_2$$

$$4NO_2+2H_2O+O_2\rightarrow 4HNO_3.$$

Process :

(i) **Catalytic Chamber** : A mixture of pure and dry ammonia and air in the ratio of 1 : 7 by volume is passed through a catalyst chamber containing platinum gauze at 800°C. The catalyst is initially heated to this temperature electrically but is subsequently maintained at this point by the heat of the reaction. Ammonia is completely oxidised to nitric oxide in this chamber.

$$4NH_3+5O_2\rightarrow 4NO+6H_2O+215\text{ Kcal.}$$

(ii) **Oxidation Chamber** : The gases are then introduced into the oxidation chamber when the temperature of the gases falls to about 200°C. Nitric oxide is now oxidised to nitrogen dioxide by the excess of atmospheric oxygen present.

$$2NO+O_2\rightarrow 2NO_2.$$

(iii) **Absorption Tower** : The gases are next passed up in absorption tower packed with quartz. Nitrogen peroxide combines with water, being sprayed from the top, in the presence of oxygen to produce nitric acid (fig. 8.9).

$$4NO_2+2H_2O+O_2 \rightarrow 4HNO_3$$

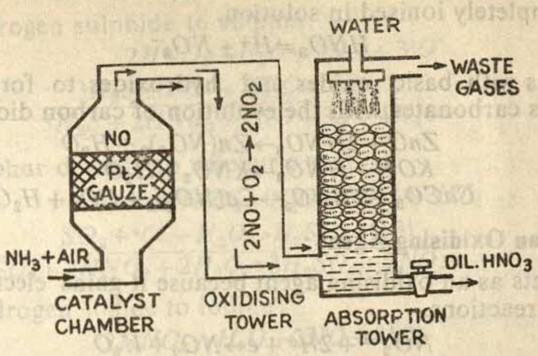


Fig. 8.9. Ostwald Process

(iv) **Concentration :** Dilute nitric acid is concentrated by distillation with concentrated sulphuric acid under reduced pressure.

(v) **Advantage** : The process being economical and efficient and is almost *invariably* employed in volume.

Physical Properties :

(a) Pure nitric acid is a colourless fuming liquid with a pungent smell. The impure acid is *yellow in colour* due to the presence of nitrogen peroxide which is produced as a result of its decomposition.

(b) HNO_3 containing a considerable quantity of dissolved nitrogen peroxide is called *fuming nitric acid* and is prepared by distilling conc. nitric acid with a little starch. The starch reduces a part of the acid to nitrogen peroxide which is absorbed by the distillate, producing fuming nitric acid.

(c) It is a highly corrosive liquid. The dilute acid produces yellow stains on the skin whereas the concentrated acid produces painful sores.

(d) It forms a constant boiling mixture which boils at 120·5°C and contains 68% nitric acid.

(e) The boiling point of pure nitric acid is 86°C.

Chemical Properties : The property of nitric acid can be discussed under three headings—

(a) Stability, (b) Acid properties, (c) Oxidising properties.

(a) *Stability :* Nitric acid is somewhat unstable and after sometime becomes yellow on account of its slight decomposition into nitrogen peroxide. On heating, it readily decomposes to give nitrogen peroxide.

$$4HNO_3 \rightleftharpoons \underset{\text{yellow}}{4NO_2}+O_2+2H_2O.$$

(b) Acid Properties : It is one of the strongest acids and is almost completely ionised in solution.

$$HNO_3 \rightleftharpoons H^+ + NO_3^-$$

It reacts with basic oxides and hydroxides to form salts. It decomposes carbonates with the evolution of carbon dioxide.

$$ZnO + 2HNO_3 \rightarrow Zn(NO_3)_2 + H_2O$$
$$KOH + HNO_3 \rightarrow KNO_3 + H_2O$$
$$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + CO_2 + H_2O$$

(c) As an Oxidising Agent :

(i) It acts as an oxidising agent because it gains electrons during a chemical reactions.

$$NO_3^{-1} + 2H^+ + e \rightarrow NO_2 + H_2O$$
$$NO_3^{-1} + 4H^+ + 3e \rightarrow NO + 2H_2O$$
$$NO_3^{-1} + 6H^+ + 5e \rightarrow \tfrac{1}{2}N_2 + 3H_2O$$
$$2NO_3^{-1} + 10H^+ + 8e \rightarrow N_2O + 5H_2O$$

(ii) It acts as a powerful oxidising agent because it readily decomposes to produce atomic oxygen.

$$2HNO_3 \rightarrow 2NO_2 + H_2O + \text{‘}O\text{’}$$

(A) It oxidises solid non-metals and metalloids to their corresponding highest oxyacids. The acid itself is reduced to nitrogen peroxide.

(i) Conc. HNO_3 oxidises carbon to Carbon dioxide.

$$2HNO_3 \rightarrow H_2O + 2NO_2 + \text{‘}O\text{’}\ [\times 2]$$
$$\underline{C + 2\text{‘}O\text{’} \rightarrow CO_2}$$
$$C + 4HNO_3 \rightarrow CO_2 + 4NO_2 + 2H_2O.$$

(ii) Conc. HNO_3 oxidises sulphur to sulphuric acid.

$$2HNO_3 \rightarrow H_2O + 2NO_2 + \text{‘}O\text{’}\ [\times 3]$$
$$\underline{S + 3\text{‘}O\text{’} + H_2O \rightarrow H_2SO_4}$$
$$S + 6HNO_3 \rightarrow H_2SO_4 + 6NO_2 + 2H_2O.$$

(iii) Conc. HNO_3 oxidises iodine to iodic acid.

$$2HNO_3 \rightarrow H_2O + 2NO_2 + \text{‘}O\text{’}\ [\times 5]$$
$$\underline{I_2 + 5\text{‘}O\text{’} + H_2O \rightarrow 2HIO_3}$$
$$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 4H_2O + 10NO_2$$

(iv) Conc. HNO_3 oxidises phosphorus to orthophosphoric acid.

$$2HNO_3 \rightarrow H_2O + 2NO_2 + \text{‘}O\text{’}\ [\times 10]$$
$$\underline{P_4 + 10\text{‘}O\text{’} + 6H_2O \rightarrow 4H_3PO_4}$$
$$P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

(B) Oxidises Inorganic Compounds : Nitric acid readily oxidises many inorganic compounds as well, being itself reduced mainly to nitric oxide.

Thus,

(i) Hydrogen sulphide to sulphur.

$$2HNO_3 \rightarrow H_2O + 2NO + 3\text{'}O\text{'}$$
$$\underline{3H_2S + 3\text{'}O\text{'} \rightarrow 3H_2O + 3S}$$
$$3H_2S + 2HNO_3 \rightarrow 2NO + 3S + 4H_2O$$

(ii) Sulphur dioxide to sulphuric acid.

$$2HNO_3 \rightarrow H_2O + 2NO + 3\text{'}O\text{'}$$
$$\underline{SO_2 + \text{'}O\text{'} + H_2O \rightarrow H_2SO_4 \; [\times 3]}$$
$$3SO_2 + 2HNO_3 + 2H_2O \rightarrow 3H_2SO_4 + 2NO.$$

(iii) Hydrogen iodide to iodine :

$$2HNO_3 \rightarrow H_2O + 2NO + 3\text{'}O\text{'}$$
$$\underline{6HI + 3\text{'}O\text{'} \rightarrow 3H_2O + 3I_2}$$
$$6HI + 2HNO_3 \rightarrow 3I_2 + 2NO + 4H_2O.$$

(iv) Ferrous sulphate to Ferric sulphate.

$$2HNO_3 \rightarrow H_2O + 2NO + 3\text{'}O\text{'}$$
$$\underline{6FeSO_4 + 3H_2SO_4 + 3\text{'}O\text{'} \rightarrow 3Fe_2(SO_4)_3 + 3H_2O}$$
$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$

(v) Acidified solution of stannous chloride to stannic chloride.

$$2HNO_3 \rightarrow H_2O + N_2O + 4\text{'}O\text{'}$$
$$\underline{SnCl_2 + 2HCl + \text{'}O\text{'} \rightarrow SnCl_4 + H_2O \; [\times 4]}$$
$$4SnCl_2 + 8HCl + 2HNO_3 \rightarrow 4SnCl_4 + N_2O + 5H_2O.$$

Action of Nitric Acid on Metals : According to Armstrong the primary action of nitric acid on metals is to evolve nascent hydrogen. But since hydrogen is a reducing agent and nitric acid is an oxidising agent, a secondary reaction takes place resulting in the reduction of nitric acid to give NO_2, NO, N_2O and NH_3. This extent of reduction of nitric acid depends upon three main factors.

(a) The nature of the metal—(b) the temperature. (c) the concentration of the acid.

If M is a monovalent metal, the reduction of nitric acid may be represented as

$$M + HNO_3 \rightarrow MNO_3 + H$$

(a) $NO_3^- + 2H^+ + e \rightleftharpoons NO_2 + H_2O$

(b) $NO_3^- + 4H^+ + 3e \rightleftharpoons NO + 2H_2O$

(c) $2NO_3^- + 10H^+ + 8e \rightleftharpoons N_2O + 5H_2O$

(d) $NO_3^{-1} + 10H^+ + 8e \rightleftharpoons NH_4^+ + 3H_2O$

Conc. and hot. HNO_3 always gives NO_2 with metals, while moderately dilute acid gives NO Very dil. acid gives N_2O and NH_3 more particularly with Zinc, Iron and Tin.

(i) Magnesium and Manganese : Give H_2 gas with dilute acid.

$$Mg+2HNO_3 \rightarrow Mg(NO_3)_2+H_2$$
$$Mn+2HNO_3 \rightarrow Mn(NO_3)_2+H_2$$

With conc. acid, however, nitrogen peroxide is formed.

(ii) In case of metals with variable valencies, such as mercury, tin and iron, dilute acid forms the *lower (-ous) nitrate* with excess of the metal and *the higher (-ic) nitrate* with excess of acid. Some important examples to illustrate the reaction of nitric acid with metals are described below.

1. Reaction with Copper and Zinc :

(a) *With concentrated nitric acid*, nitrogen dioxide is produced.

$$Cu+2HNO_3 \rightarrow Cu\,(NO_3)_2+2H$$
$$\underline{H+HNO_3 \rightarrow NO_2+H_2O\ [\times 2]}$$
$$Cu+4HNO_3 \rightarrow Cu\,(NO_3)_2+2NO_2+2H_2O$$

Similarly $$Zn+4HNO_3 \rightarrow Zn\,(NO_3)_2 \times 2NO_2+2H_2O$$
$$[Zn+4H^+ +2NO_3^- \rightarrow Zn^{+2}+2NO_2+2H_2O]$$

(b) *With Moderate dilute acid*, nitric oxide is obtained.

$$Cu+2HNO_3 \rightarrow Cu\,(NO_3)_2+2H\ [\times 3]$$
$$\underline{3H+HNO_3 \rightarrow NO+2H_2O\quad [\times 2]}$$
$$3Cu+8HNO_3 \rightarrow 3Cu\,(NO_3)_2+2NO+4H_2O$$

Similarly $$3Zn+8HNO_3 \rightarrow 3Zn\,(NO_3)_2+2NO+4H_2O$$
$$[3Zn+8H^+ +2NO_3^- \rightarrow 3Zn^{+2}+2NO+4H_2O]$$

(c) *With very dilute acid*, nitrous oxide is obtained.

$$Cu+2HNO_3 \rightarrow Cu\,(NO_3)_2+2H\ [\times 4]$$
$$\underline{8H+2HNO_3 \rightarrow N_2O+5H_2O}$$
$$4Cu+10HNO_3 \rightarrow 4Cu\,(NO_3)_2+N_2O+5H_2O$$

Similarly $$4Zn+10HNO_3 \rightarrow 4Zn\,(NO_3)_2+N_2O+5H_2O$$
$$[4Zn+10H^+ +2NO_3^- \rightarrow 4Zn^{++}+N_2O+5H_2O]$$

(d) *Zinc gives ammonium nitrate*, with very dil. acid.

$$Zn+2HNO_3 \rightarrow Zn\ (NO_3)_2+2H\ \ [\times 4]$$
$$\underline{2HNO_3+8\text{'}H\text{'} \rightarrow NH_4NO_3+3H_2O}$$
$$4Zn+10HNO_3 \rightarrow 4Zn\,(NO_3)_2+NH_4NO_3+3H_2O$$
$$[4Zn+10H^+ +NO_3^- \rightarrow 4Zn^{+2}+NH_4^+ +3H_2O]$$

2. Reaction with Mercury :

(a) *With dilute acid* it gives mercurous nitrate with evolution of nitric oxide.

$$\begin{array}{c} 2Hg+2HNO_3 \rightarrow Hg_2(NO_3)_2+2H\ [\times 3] \\ 3H+HNO_3 \rightarrow NO+2H_2O\ [\times 2] \\ \hline 6Hg\quad 8HNO_3 \rightarrow 3Hg_2(NO_z)_2+2NO+4H_2O \\ [6Hg+8H^+ +2NO_3^- \rightarrow 3Hg_2^{++}+2NO+4H_2O] \end{array}$$

(b) *With conc. acid*, mercuric nitrate and nitrogen peroxide are formed.

$$\begin{array}{c} Hg+2HNO_3 \rightarrow Hg\ (NO_3)_2+2H \\ H+HNO_3 \rightarrow NO_2+H_2O\ [\times 2] \\ \hline Hg+4HNO_3 \rightarrow Hg\ (NO_3)_2+2NO_2+2H_2O \\ [Hg+4H^+ +2NO_3^- \rightarrow Hg^{++}+2NO_2+2H_2O] \end{array}$$

3. Reaction with Iron :

(a) It gives ammonium nitrate and ferrous nitrate with cold and dilute nitric acid.

$$\begin{array}{c} Fe+2HNO_3 \rightarrow Fe\ (NO_3)_2+2H\ [\times 4] \\ 2HNO_3+8H \rightarrow NH_4NO_3+3H_2O \\ \hline 4Fe+10HNO_3 \rightarrow 4Fe\ (NO_3)_2+NH_4NO_3+3H_2O \\ [4Fe+10H^+ +NO_3^- \rightarrow 4Fe^{++}+NH_4^+ +3H_2O] \end{array}$$

(b) It gives Ferric nitrate and nitric oxide with moderate HNO_3.

$$\begin{array}{c} Fe+6HNO_3 \rightarrow Fe\ (NO_3)_3+3NO_2+3H_2O \\ [Fe+6H^+ +3NO_3^- \rightarrow Fe^{+3}+3NO_2+3H_2O] \end{array}$$

4. *Reaction with silver* : (a) Nitric oxide is produced on reaction with dilute acid.

$$\begin{array}{c} Ag+HNO_3 \rightarrow AgNO_3+H\ [\times 3] \\ HNO_3+3H \rightarrow NO+H_2O \\ \hline 3Ag+4HNO_3 \rightarrow 3AgNO_3+NO+2H_2O \\ [3Ag+4H^+ +NO_3^{-1} \rightarrow 3Ag^+ +NO+2H_2O] \end{array}$$

(b) With conc. acid, its gives nitrogen peroxide.

$$\begin{array}{c} Ag+HNO_3 \rightarrow AgNO_3+H \\ HNO_3+H \rightarrow NO_2+H_2O \\ \hline Ag+2HNO_3 \rightarrow AgNO_3+NO_2+H_2O \\ [Ag+2H^+ +NO_3^- \rightarrow Ag^+ +NO_2+H_2O] \end{array}$$

5. *Reaction with Tin* : (a) With cold and dilute acid, it gives stannous nitrate and ammonium nitrate :

$$\begin{array}{c} Sn+2HNO_3 \rightarrow Sn\ (NO_3)_2+2H\ [\times 4] \\ 2HNO_3+8H \rightarrow NH_4NO_3+3H_2O \\ \hline 4Sn+10HNO_3 \rightarrow 4Sn\ (NO_3)_2+NH_4NO_3+3H_2O \\ [4Sn+10H^+ +NO_3^- \rightarrow 4Sn^{+2}+NH_4^+ +3H_2O] \end{array}$$

(b) With conc. and hot acid, it gives metastannic acid and nitrogen peroxide.

$$\begin{array}{l} 2HNO_3 \rightarrow H_2O + 2NO_2 + O\ [\times 2] \\ \underline{Sn + 2\text{'}O\text{'} + H_2O \rightarrow H_2SnO_3} \\ Sn + 4HNO_3 \rightarrow H_2SnO_3 + 4NO_2 + H_2O \\ H_2SnO_3 \rightarrow SnO_2 + H_2O \end{array}$$

6. *Reaction with Arsenic and Antimony* : They are converted to their oxyacids by the action of conc. acid.

$$As + 5HNO_3 \rightarrow \underset{\text{Arsenic acid}}{H_3AsO_4} + 5NO_2 + H_2O$$

$$Sb + 5HNO_3 \rightarrow \underset{\text{Antimonic acid}}{H_3SbO_4} + 5NO_2 + H_2O$$

7. *Reaction with Cobalt and Nickel* : They give nitric oxide with dilute acid.

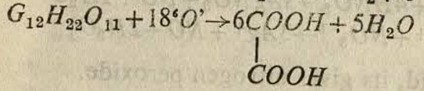
$$3Co + 8HNO_3 \rightarrow 3Co\ (NO_3)_2 + 2NO + 4H_2O.$$

Note : Conc. acid renders iron, aluminium, chromium, cobalt and nickel passive. This is probably due to the formation of a thin film of the oxide on the surface of the metal, thereby preventing the metal from coming into contact with the metal.

8. *Reaction with organic compounds* : Organic compounds are either oxidised or nitrated when heated with nitric acid.

(i) *Oxidations* : It oxidises cane-sugar (sucrose) to oxalic acid.

$$2HNO_3 \rightarrow H_2O + 2NO_2 + O$$



$$G_{12}H_{22}O_{11} + 18\text{'}O\text{'} \rightarrow 6\begin{array}{c} COOH \\ | \\ COOH \end{array} + 5H_2O$$

Oxalic acid

(ii) *Nitration* : Concentrated nitric acid reacts with benzene and its derivatives in the presence of concentrated sulphuric acid. Nitro derivatives are produced.

$$\underset{\text{Benzene}}{C_6H_5H} + \underset{\text{Nitric acid}}{OHNO_2} \rightarrow \underset{\text{Nitro benzene}}{C_6H_5NO_2} + H_2O$$

Note : *Aqua Regia* : It is a mixture of conc. HCl and conc. HNO_3 in the ratio of 3 : 1. It even dissolves the noble metals, gold and platinum. Nascent chlorine is produced due to interaction of acids and reacts with these metals to form soluble chlorides.

$$3HCl + HNO_3 \rightarrow \underset{\text{Nitrosyl chloride}}{NOCl} + 2\text{'}Cl\text{'} + 2H_2O$$

$$Au + 3\,\text{'}Cl\text{'} \rightarrow \underset{\text{Auric chloride}}{AuCl_3}$$

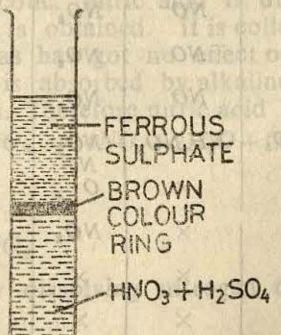
$$Pt + 4\,\text{'}Cl\text{'} \rightarrow \underset{\text{Platinum chloride}}{PtCl_4}$$

Uses : 1. It is used in the manufacture of :

(a) rayon, (b) fertilisers, (c) explosives such as T. N. T., picric acid, trinitroglycerine (T.N.G.), dynamite, Trinitrobenzene (T.N.B.) and gun cotton.

2. In electroplating. 3. In purification of gold and silver. 4. In the laboratory reagent.

Test for Nitric acid (or Nitrate) : When conc. H_2SO_4 is added slowly to a solution containing nitric acid or nitrate (NO_3^-) and ferrous sulphate a brown ring is formed at the junction of H_2SO_4 and nitrate solution. Nitric oxide (NO) produced in the reaction is absorbed by $FeSO_4$ solution and a compound $FeSO_4.xNO$ or $[Fe(H_2O)_5NO]\,SO_4$ is obtained.



$$2HNO_3 = H_2O + 2NO + 3\text{'}O\text{'}$$

$$\underline{6FeSO_4 + 3H_2SO_4 + 3\text{'}O\text{'} \rightarrow 3Fe_2\,(SO_4)_3 + 3H_2O}$$

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

$$FeSO_4 + NO + 5H_2O \rightarrow \underset{\text{Brown ring}}{[Fe(H_2O)_5NO]SO_4}$$

Structure of Nitric acid : The electron dots formula of HNO_3 is shown in the chapter of electronic theory of valency.

Remember : Reaction of HNO_3 with metals and non-metals. The table below shows the reactions of nitric acid under different conditions with metals and non-metals both :

Elements	*15% HNO_3 Very dilute*	*30% HNO_3 Dilute*	*50% HNO_2 Moderate*	*Conc. HNO_3*	*Vapour*	*Remark*
C	×	×	×	NO_2	×	CO_2+H_2O
P	×	×	×	NO_2	×	$H_3PO_4+H_2O$
S	×	×	×	NO_2	×	$H_2SO_4+H_2O$
I	×	×	×	NO_2	×	HIO_3+H_2O
Zn	NH_4NO_3	N_2O	NO	NO_2	×	$Zn\,(NO_3)_2+H_2O$
Fe	NH_4NO_3	NH_4NO_3	NO	Passive *	×	$Fe(NO_3)_2+H_2O$ $Fe(NO_3)_3+H_2O$*
Cu	×	N_2O	NO	NO_2	N_2	$\rightarrow CuO+H_2O$ $Cu(NO_3)_2+H_2O$ (Rest)
Hg	×	×	NO	NO_2	×	$Hg_2(NO_3)_2+H_2O(NO)$ $Hg(NO_3)_2+H_2O(NO_2)$
Ag	×	×	NO	NO_2	×	$Ag(NO_3)+H_2O$
Sn	×	NH_4NO_3	NH_4NO_3	NO_2	×	$Sn(NO_3)_2+H_2O$ (NH_4NO_3) $H_2SnO_3+H_2O\,(NO_2)$
As	×	×	×	NO_2	×	$H_3AsO_4+H_2O$
Sb	×	×	×	NO_2	×	$H_3SbO_4+H_2O$
Mg	×	H_2	×	×	×	$Mg\,(NO_3)_2$
Mn	×	H_2	×	×	×	$Mn\,(NO_3)_2$

Action of Heat on Nitrates :

(1) $$\underset{\text{Amm. Nitrate}}{NH_4NO_3} \xrightarrow[\text{Low Temp.}]{\text{Heat}} N_2O+2H_2O$$

(2) $$\underset{(M=Na,\ K)}{MNO_3} \xrightarrow[\text{heat}]{\text{Strong}} MNO_2+O_2$$

(3) $$AgNO_3, Hg(NO_3)_2 \xrightarrow{\text{heat}} \text{Metal} + NO_2 + O_2$$
(Metal = Ag or Hg)

(4) All other metal nitrates $\xrightarrow{\text{heat}}$ Metal oxide + $NO_2 + O_2$

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2.$$

To prove that HNO_3 contains H_2, N_2 and oxygen :

1. **Hydrogen :** When Mg is treated with dil. nitric acid then a colourless and odourless gas is obtained. It is collected by displacement of water. It burns with blue flame. It is absorbed by heated Pd Hence the gas is hydrogen. Since Mg does not contain hydrogen, hence it must have come from nitric acid. Therefore, nitric acid contains hydrogen.

$$Mg + 2HNO_3 \rightarrow Mg(NO_3)_2 + H_2.$$

2. **Nitrogen :** When nitric acid vapour is passed over red hot copper turning then a colourless and odourless gas is obtained. This is collected over water. It is inactive gas and it is absorbed by heated Mg. Hence the gas is nitrogen. Therefore, nitric acid contains nitrogen.

$$5Cu + 2HNO_3 \rightarrow 5CuO + N_2 + H_2O.$$

3. **Oxygen :** When conc. nitric acid is dropped over red hot pumice stone then a gas is obtained. It is collected by the displacement of water. The gas has got no effect on litmus paper and it helps combustion. It is absorbed by alkaline pyragallol solution. Hence the gas is oxygen. Therefore nitric acid contains oxygen.

$$4HNO_3 \rightarrow 4NO_2 + 2H_2O + O_2.$$

8.5. Nitrous Acid

Molecular Formula HNO_2 Molecular Wt. 47

Preparation : 1. By dissolving nitrogen trioxide in ice cold water.

$$N_2O_3 + H_2O \rightarrow 2HNO_2$$

2. By the action of dilute HCl or H_2SO_4 with sodium or potassium nitrite.

$$NaNO_2 + HCl \rightarrow NaCl + HNO_2$$

$$KNO_2 + H_2SO_4 \rightarrow KHSO_4 + HNO_2$$

3. **Laboratory Method :** Pure dilute nitrous acid can be prepared by treating ice-cold solutions of calculated quantities of barium nitrite and sulphuric acid. The precipitated barium sulphate is filtered off :

$$Ba(NO_2)_2 + H_2SO_4 \rightarrow BaSO_4 \downarrow + 2HNO_2.$$

Properties :

(a) Its aqueous solution is blue in colour.

(b) *Stability* : It is an unstable acid. Its solution on standing undergoes auto-oxidation forming nitric acid and nitric oxide.

$$\begin{array}{l} 2HNO_2 \rightarrow H_2O + NO + `O' \\ \underline{HNO_2 + `O' \rightarrow HNO_3} \\ 3HNO_2 \rightarrow HNO_3 + 2NO + H_2O. \end{array}$$

(c) *Acidic Properties* : It is a weak monobasic acid. It reacts with alkalies to form salts. Salts of nitrous acid are called Nitrites.

$$NaOH + HNO_2 \rightarrow NaNO_2 + H_2O.$$

(d) *As Oxidising Agent* : (i) It gains electrons during a chemical reaction, hence it acts as an oxidising agent.

$$\begin{array}{l} HNO_2 \rightarrow H^+ + NO_2^- \\ \underline{NO_2^- + 2H^+ + e \rightarrow NO + H_2O} \\ HNO_2 + H^+ + e \rightarrow NO + H_2O. \end{array}$$

(ii) When HNO_2 reacts with reducing agents, it gives "NO". It acts as an oxidising agent because it decomposes to produce atomic oxygen.

$$2HNO_2 \rightarrow H_2O + 2NO + `O'$$

(a) *Hydrogen Sulphide to Sulphur :*

$$\begin{array}{l} 2HNO_2 \rightarrow H_2O + 2NO + `O' \\ \underline{H_2S + `O' \rightarrow H_2O + S} \\ H_2S + 2HNO_2 \rightarrow S + 2NO + 2H_2O. \\ (S^{-2} + 2NO_2^- + 4H^+ \rightarrow S + 2NO + 2H_2O) \end{array}$$

(b) *Sulphur dioxide to Sulphuric acid :*

$$\begin{array}{l} 2HNO_2 \rightarrow H_2O + 2NO + `O' \\ \underline{SO_2 + `O' + H_2O \rightarrow H_2SO_4} \\ SO_2 + 2HNO_2 \rightarrow H_2SO_4 + 2NO \\ (SO_2 + 2NO_2^- + 2H^+ \rightarrow SO_4^{-2} + 2NO) \end{array}$$

(c) *Potassium iodide to Iodine :*

$$\begin{array}{l} 2HNO_2 \rightarrow H_2O + 2NO + `O' \\ \underline{2KI + H_2O + `O' \rightarrow 2KOH + I_2} \\ 2KI + 2HNO_2 \rightarrow 2KOH + 2NO + I_2 \\ (2I^- + 2NO_2^- + 2H^+ \rightarrow OH^- + 2NO + I_2) \end{array}$$

(d) *$SnCl_2$ to $SnCl_4$:*

$$\begin{array}{c} 2HNO_2\rightarrow H_2O+2NO+\text{‘O’} \\ SnCl_2\times 2HCl+\text{‘O’}\rightarrow SnCl_4+H_2O \\ \hline SnCl_2+2HCl+.2HNO_2\rightarrow SnCl_4+2NO+2H_2O \end{array}$$

$$(Sn^{+2}+2NO_2^{-}+4H^{+}\rightarrow Sn^{+4}+2NO+2H_2O)$$

(E) As Reducing Agent : (i) It loses electrons during a Chemical reaction.

$$\begin{array}{c} HNO_2\rightarrow H^{+}+NO_2^{-} \\ NO_2^{-}+H_2O\rightarrow NO_3^{-1}+2H^{+}+2e \\ \hline HNO_2+H_2O\rightarrow 3H^{+}+NO_3^{-1}+2e \end{array}$$

(ii) It acts as a reducing agent as well because of the case with which it can be oxidised to Nitric acid.

$$HNO_2+O\rightarrow HNO_3$$

It reduces :

(a) *Chlorine and Bromine to HCl and HBr* **respectively :**

$$\begin{array}{c} X_2+H_2O\rightarrow 2HX+\text{‘O’} \\ HNO_2+O\rightarrow HNO_3 \\ \hline HNO_2+X_2+H_2O\rightarrow HNO_3+2HX.(X=Cl,\ Br,\ I) \end{array}$$

$$(NO_2^{-}+X_2+H_2O\rightarrow NO_3^{-1}+2X^{-1}+2H^{+})$$

(b) *Potassium Permanganate to Manganous salt :*

$$\begin{array}{ll} & 2KMnO_4+3H_2SO_4\rightarrow K_2SO_4+2MnSO_4+3H_2O+5\text{‘O’} \\ & 5HNO_2+5\text{‘O’}\rightarrow 5HNO_3 \\ \hline & 2KMnO_4+3H_2SO_4+5HNO_2 \\ \text{Pink} & \rightarrow \underbrace{5HNO_3+2MnSO_4+3H_2O+K_2SO_4}_{\text{Colourless}} \end{array}$$

$$(2MnO_4^{-}+5NO_2^{-}+6H^{+}\rightarrow 5NO_3^{-}+2Mn^{++}+3H_2O)$$

(c) *H_2O_2 to water :*

$$H_2O_2+HNO_2\rightarrow HNO_3+H_2O$$

$$(O_2^{-2}+NO_2^{-1}+2H^{+}\rightarrow NO_3^{-1}+H_2O)$$

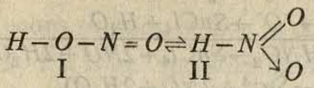
(d) *Acidified solulion of Potassium dichromate* (orange) *to green $Cr_2(SO_4)_3$:*

$$\begin{array}{l} K_2Cr_2O_7+4H_2SO_4\rightarrow Cr_2(SO_4)_3+K_2SO_4+4H_2O+3\text{‘O’} \\ 3HNO_2+3\text{‘O’}\rightarrow 3HNO_3 \\ \hline K_2Cr_2O_7+4H_2SO_4+3HNO_2 \\ \qquad\rightarrow K_2SO_4+Cr_2(SO_4)_3+4H_2O+3HNO_3 \end{array}$$

$$(Cr_2O_7^{-2}+3NO_2^{-1}+8H^{+}\rightarrow 3NO_3^{-1}+2Cr^{+3}+4H_2O)$$

Uses : It is used in the manufacture of azo dyes.

Structure of Nitrous Acid : It has got resonating structure. It exhibits tautomerism i.e. is equilibrium mixture of I and II forms.



Test for Nitrous Acid : When HNO_2 is added to mixture of $FeSO_4$ solution and H_2SO_4 then whole solution turns brown.

Test for Nitrites : (i) When dil. mineral acid (HCl, H_2SO_4) is added to nitrites and the product is added to moist starch iodide paper then blue colour is obtained. It indicates the presence of nitrites.

(ii) When acidified solution of nitrite is added to $KMnO_4$ solution then its violet colour is decolourised.

(iii) When acidified solution of nitrite is added to $K_2Cr_2O_7$ solution then its orange colour turns green.

Action of Heat on Nitrites : They are generally more stable than nitrates. All metal nitrites except NH_4NO_2 do not decompose on heating.

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

$$KNO_2 \xrightarrow{\text{heat}} \text{No reaction.}$$

8.6. Oxides of Nitrogen

Nitrogen forms five well-defined oxides. These are :

Oxidation State	+1	+2	+3	+4	+5
Formula of Oxides	N_2O	NO	N_2O_3	NO_2 or N_2O_4	N_2O_5
Name and Nature	Laughing gas, Neutral	Nitric Oxide, Neutral	Anhydride of HNO_2, Acidic	Acidic	Anhydride of HNO_3, Acidic

8.7. Nitrous Oxide (N_2O)

Preparation :

Laboratory Method : It is prepared in the laboratory by heating ammonium nitrate.

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

The method is not used for the preparation of N_2O in the laboratory because it explodes at 218°C. It is therefore, better to use a mixture of sodium nitrate and NH_4Cl.

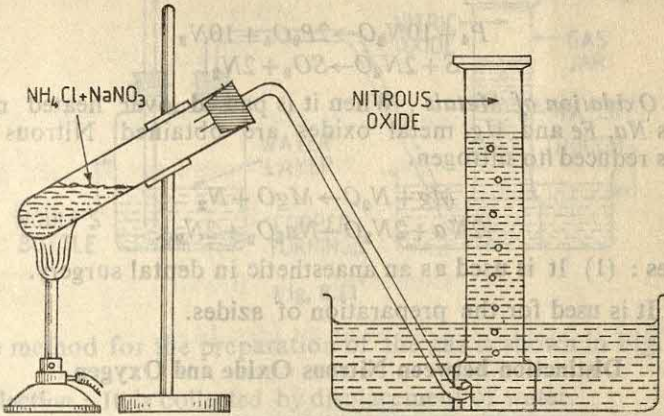


Fig. 8.10

$$\begin{aligned} &NaNO_3 + NH_4Cl \rightarrow NH_4NO_3 + NaCl \\ &NH_4NO_3 \rightarrow N_2O + 2H_2O \\ \hline &NaNO_3 + NH_4Cl = N_2O + 2H_2O + NaCl \end{aligned}$$

Collection : It is collected over hot water as it is fairly soluble in cold water.

Pure N_2O : The gas obtained above contains oxides of nitrogen as impurities. The impure gas is passed through ferrous sulphate solution to remove oxides of Nitrogen. It is next passed through caustic soda solution to remove vapours of nitric acid and chlorine. The gas is finally dried by bubbling it through concentrated sulphuric acid.

Physical Properties : (a) It is a colourless gas with a faint, sweet odour and taste.

(b) It is heavier than air.

(c) It is fairly soluble in cold water but its solubility *decreases appreciably with increase in the temperature of water.*

(d) When inhaled in moderate quantities, it induces hysterical laughter. Hence it is also named as *laughing gas.*

Chemical Properties :

(a) *Stability :* It is not a very stable compound on heating, it decomposes into its elements.

$$2N_2O \rightarrow 2N_2 + O_2 + 39 \text{ K cals.}$$

(b) *Supporter of combustion :* It is an incombustible gas. Since the gas readily decomposes to give oxygen, it supports the combustion of a glowing splinter of wood and brightly burning sulphur and phosphorus.

$$P_4+10N_2O\rightarrow 2P_2O_5+10N_2$$
$$S+2N_2O\rightarrow SO_2+2N_2$$

(c) *Oxidation of Metals :* When it is passed over heated metals, such as Na, Fe and Mg, metal oxides are obtained. Nitrous oxide itself is reduced to nitrogen.

$$Mg+N_2O\rightarrow MgO+N_2$$
$$2Na+2N_2O\rightarrow Na_2O_2+2N_2.$$

Uses : (1) It is used as an anaesthetic in dental surgery.

(2) It is used for the preparation of azides.

Distinction between Nitrous Oxide and Oxygen :

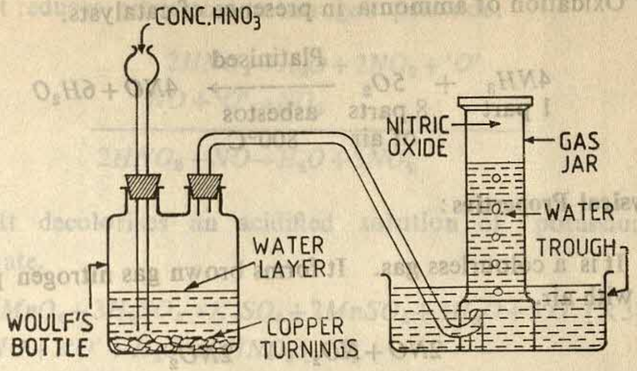
N_2O	O_2
1. A colourless gas with sweetish test and pleasant smell.	1. A colourless gas with no taste or smell.
2. It is not absorbed by sodium pyrogallate solution.	2. It is absorbed by sodium pyrogallate solution.
3. It produces anaesthesia if inhaled in excess and causes laughter if inhaled in small quantities.	3. Oxygen does not produce such effects.
4. Fairly soluble in cold water, but insoluble in hot water.	4. Sparingly soluble in cold water and still less so in hot water.
5. It does not have any action on metals at ordinary temperature.	5. Corrosion of many metals takes place by moist oxygen at ordinary temperature e. g., rusting of iron takes place at all temperatures.

8.8. Nitric Oxide (NO)

Preparation :

Laboratory Method : It is prepared by the action ofcold dilute nitric acid on copper turnings.

$$Cu+2HNO_3\rightarrow Cu(NO_3)_2+2H\ [\times 3]$$
$$\underline{HNO_3+3\text{'}H\text{'}\rightarrow NO+2H_2O\ [\times 2]}$$
$$3Cu\quad 8HNO_3\rightarrow 3Cu(NO_3)_2+2NO+4H_2O$$



Fig, 8.11

The method for the preparation of the gas is shown in Fig. 8.11

Collection : It is collected by displacement of water.

Pure Nitric oxide : To purify, the gas is passed through ferrous sulphate solution. Nitric oxide is dissolved by ferrous sulphate solution due to the formation of nitroso ferrous sulphate. The impurites present in the gas are not dissolved. Nitric oxide is recovered by heating nitroso ferrous sulphate.

$$\underset{\text{Impure}}{FeSO_4 + NO} \rightarrow \underset{\substack{\text{Nitroso-}\\\text{Ferrous Sulphate}}}{FeSO_4.NO} \rightarrow FeSO_4 + \underset{\text{Pure}}{NO}$$

Other Methods :

(a) When air is passed through an electric arc, nitrogen and oxygen combine to form "NO"

$$N_2 + O_2 \rightleftharpoons 2NO - 43{\cdot}2 \text{ Kcals.}$$

(b) By heating a mixture of potassium nitrate and ferrous sulphate with dilute sulphuric acid.

$$KNO_3 + H_2SO_4 \rightarrow KHSO_4 + HNO_3 \; [\times 2]$$
$$HNO_3 \rightarrow H_2O + 2NO + 3\text{‘}O\text{’}$$
$$2FeSO_4 + H_2SO_4 + \text{‘}O\text{’} \rightarrow Fe_2(SO_4)_3 + H_2O \; [\times 3]$$
$$\overline{2KNO_3 + 6FeSO_4 + 5H_2SO_4 \rightarrow 2KHSO_4 + 3Fe_2(SO_4)_3 + 2NO + 4H_2O.}$$

(c) Oxidation of ammonia in presence of catalysts.

$$\underset{\text{1 part}}{4NH_3} + \underset{\substack{\text{8 parts}\\\text{of air}}}{5O_2} \xrightarrow[\substack{\text{asbestos}\\800°C}]{\text{Platinised}} 4NO+6H_2O$$

Physical Properties:

(a) It is a colourless gas. It forms brown gas nitrogen peroxide (NO_2) with air.

$$\underset{\text{Colourless}}{2NO+NO_2} \rightarrow \underset{\text{Brown}}{2NO_2}$$

(b) It is slightly heavier than air ($D=14{\cdot}4$).

(c) It is very slightly soluble in water.

(d) It is liquefied with difficulty.

Chemical Properties:

(a) *Stability* : It is the most stable oxide of nitrogen. It starts decomposition at 500°C.

$$2NO \rightarrow N_2+O_2$$

(b) *Supporter of combustion* : It is an incombustible gas. On account of its stability it acts as a supporter of combustion in a few cases only. Boiling sulphur, brightly burning phosphorus, and red hot charcoal are oxidised by it.

$$S+2NO \rightarrow SO_2+N_2$$
$$P_4+10NO \rightarrow 2P_2O_5+5N_2$$
$$C+2NO \rightarrow CO_2+N_2$$

(c) *Combination with oxygen* : It directly combines with oxygen at the room temperature to form brown vapours of nitrogen peroxide.

$$2NO+O_2 \rightarrow 2NO_2$$

(d) *As reducing agent* : On account of the readiness with which it combines with oxygen, it acts as a reducing agent.

(i) It reduces nitric acid to nitrogen peroxide.

$$\begin{array}{l} 2HNO_3 \rightarrow H_2O + 2NO_2 + \text{'}O\text{'} \\ NO + \text{'}O\text{'} \rightarrow NO_2 \\ \hline 2HNO_3 + NO \rightarrow H_2O + 3NO_2 \end{array}$$

(ii) It decolorises an acidified solution of potassium permanganate.

$$\begin{array}{l} 2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5\text{'}O\text{'} \ [\times 3] \\ 2NO + 3\text{'}O\text{'} + H_2O \rightarrow 2HNO_3 \ [\times 5] \\ \hline 6KMnO_4 + 9H_2SO_4 \\ \qquad + 10NO \rightarrow 3K_2SO_4 + 6MnSO_4 + 4H_2O + 10HNO_3 \end{array}$$

(e) *Reaction with chlorine* : It combines with chlorine to form nitrosyl chloride.

$$2NO + Cl_2 \rightarrow 2NOCl$$

(f) *Reaction with Ferrous sulphate* : When it is passed through ferrous sulphate solution, the solution becomes dark due to the formation of nitroso ferrous sulphate. Nitroso ferrous sulphate decomposes on heating to give back nitric oxide.

$$FeSO_4 + NO \rightarrow FeSO_4.NO \xrightarrow{\text{heat}} FeSO_4 + NO$$

(g) *As oxidising agent :* It acts as an oxidising agent in certain reactions.

(i) It oxidises hydrogen sulphide to sulphur.

$$H_2S + 2NO \rightarrow H_2O + N_2O + S$$

(ii) It oxidises sulphurous acid to sulphuric acid.

$$H_2SO_3 + 2NO \rightarrow H_2SO_4 + N_2O$$

Uses : (i) In the preparation of HNO_3.

(ii) As catalyst in the manufacture of H_2SO_4 by chamber process.

8.9. Other Oixdes of Nitrogen

Terms	*Nitrogen trioxide or sesquioxide* N_2O_3	*Nitrogen peroxide, Nitrogen dioxide, Nitrogen tetra oxide—*N_2O_4	*Nitrogen pentoxide, Nitric anhydride* N_2O_5
PREPARATION	(a) $NO+NO_2 \xrightarrow[-30^\circ C]{\text{Cooled to}} N_2O_3$ (b) Arsenious oxide is heated with 50% HNO_3. The evolved gas condenses to a blue liquid on passing through a U-tube cooled in freezing mixture. $As_2O_3+2HNO_3+2H_2O \rightarrow 2H_3AsO_4+N_2O_3$	(a) $2NO+O_2 \xrightarrow[\text{direct}]{\text{air}} N_2O_5$ (b) By heating copper turnings with conc nitric acid. $Cu+4HNO_3+Cu(NO_3)_2 \rightarrow 2NO_2+2H_2O$ (c) By heating lead nitrate. $2Pb(NO_3)_2 \rightarrow 2PbO+4NO_2+O_2$	(a) By passing ozone (O_3) through liquid nitrogen dioxide. $N_2O_4+O_3 \rightarrow N_2O_5+O_2$ (b) By distilling a mixture of nitric acid and P_2O_5 at 30°C. $2HNO_3 \rightarrow P_2O_5+N_2O_5+2HPO_3$ Meta-phosphoric acid.
PROPERTIES :			
(a) Colour —	Blue liquid at —20°C	Reddish brown colour	Colourless, crystalline solid.
(b) Smell —	No smell	Pungent odour	No smell.
(c) Stability —	$N_2O_3 \xrightarrow{\text{R T.P.}} NO+NO_2$	$N_2O_4 \xrightarrow[140^\circ C]{} 2NO_2$	Unstable. It decomposes on heatingt to give reddish brown fumes of nitrogen peroxide. $2N_2O_5 \rightarrow 4NO_2+O_2$
(d) Reaction with water	It is the anhydride of HNO_2. Hence it gives HNO_2 with water. $N_2O_3+H_2O \rightarrow 2HNO_2$	It is the mixed anhydride of nitrous and nitric acid Hence it gives HNO_2 and HNO_3 with water. $2NO_2+H_2O \rightarrow HNO_2+HNO_3$	It is the anhydride of HNO_3. Hence it is soluble in water. $N_2O_5+H_2O \rightarrow 2HNO_3$
(e) Reaction with alkalies	$N_2O_3+2KOH \rightarrow 2KNO_2+H_2O$ Pot. nitrite	$2NO_2+2KOH \rightarrow KNO_2+KNO_3+H_2O$	$KOH+N_2O_5 \rightarrow 2KNO_3+H_2O$
(f) As Oxidising agent	×	(a) $2FeSO_4+H_2SO_4+NO_2 \rightarrow Fe_2(SO_4)_3+H_2O+NO$ (b) $2KI+NO_2 \rightarrow 2KNO_2+I_2$ ×	(a) Rubber + $N_2O_5 \rightarrow$ violent reaction (b) Cork + $N_2O_5 \rightarrow$,, ,, ×

8.10. Phosphorus (P)

Atomic Number—15 Mass Number—31

Electronic configuration—$1s^2 2s^2 2p^6 3s^2 3p_x^1 p_y^1 p_z^1$.

Sources of Phosphorous : The chief source of phosphorous is calcium phosphate, $Ca_3(PO_4)_2$, which is found in the following minerals :

(a) Phosphorite : $Ca_3(PO_4)_2 . Ca(OH)_2$

(b) Chlorapatite : $3Ca_3(PO_4)_2 . CaCl_2$

(c) Fluorapatite : $3Ca_3(PO_4)_2 . CaF_2$

(d) Bones : Mainly contain $Ca_3(PO_4)_2$.

Manufacture of White or Yellow Phosphorous :

It is generally obtained either from bone ash or phosphorite mineral. To get bone ash, bones are well-powdered and washed with Benzene or carbon disulphide to free it from greasy materials. These bones are then boiled with water and subjected to destructive distillation whereby bone oil distills over leaving behind animal charcoal. The latter is burnt in air to get bone ash which contains about 60% calcium phosphate.

There are two main processes to get phosphorous :

(i) Old or Retort Process : The mixture containing Bone ash, coke and conc. H_2SO_4 is placed in a fire clay retorts and distilled. The vapours of phosphorous are condensed under water into a waxy solid. The reaction takes place as follows :

(a) $$\underset{\text{Bone ash}}{Ca_3(PO_4)_2} + 3H_2SO_4 \longrightarrow 3CaSO_4\downarrow + \underset{\text{(In soln.)}}{2H_3PO_4}$$

(b) $$\underset{\substack{\text{Ortho-}\\\text{phosphoric acid}}}{H_3PO_4} \xrightarrow{\text{Evaporated}} \underset{\substack{\text{Meta-phosphoric}\\\text{acid}}}{HPO_3} + H_2O$$

(c) $$2HPO_3 + 5C\text{ (coke)} \xrightarrow[\text{retort}]{\text{heat in}} 5CO\uparrow + \underbrace{2P\downarrow + H_2O}_{\text{Water}}$$

(d) $$4P \longrightarrow P_4.$$

(ii) **Modern Electrical Process :** In this process : (a) Bone ash or powdered phosphoric mineral, $Ca_3(PO_4)_2$ is mixed with sand (Fig. 8.12) and coke (mixture is called charge) is fed into electric furnace through hopper. (b) The temperature of furnace is maintained to 1200⁰ - 1500°C by striking an electric arc between two carbon electrodes in the furnace. (c) At this temperature, calcium phosphate first reacts with silica to form calcium silicate, $CaSiO_3$ (Slag), and phosphorous pentoxide (P_2O_5). Now P_2O_5 is reduced by carbon to give phosphorous and carbon monoxide.

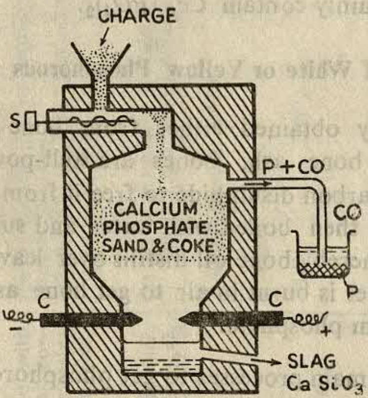


Fig. 8.12

$$\underset{\text{Bone}}{Ca_3(PO_4)_2 + 3SiO_2} \xrightarrow[\text{arc1200°C}]{\text{Electric}} \underset{\text{Cal. Silicate (Slag)}}{3CaSiO_3\downarrow + P_2O_5}$$

$$P_2O_5 + 5C \longrightarrow 2P\underbrace{\downarrow + 5CO}_{\text{Water}}\uparrow$$

$$4P = P_4$$

(d) The vapour of phosphorous alongwith CO gas passes out through the exit and is passed into water. Phosphorous gets condensed into waxy solid while CO passes away (insoluble in water). Calcium silicate is left behind in furnace in the fused state and is tapped off from the slag hole.

FLOW SHEET : FOR THE MANUFACTURE OF WHITE PHOSPHOROUS

(i) **Old Process :**

$$\text{Bone} \xrightarrow[\text{with } C_6H_6 \text{ or } CS_2]{\text{Powdered, washed}} \text{Bone free from greasy material}$$

$$\Big\downarrow \text{ Burnt in air}$$

$$\underset{\text{(kept in water)}}{\text{White } P_4} \xleftarrow[\text{coke and conc. } H_2SO_4 \text{ in a retort distilled}]{\text{Mixed with}} \text{Bone ash}$$

(ii) **Modern Electrical Process :**

$$\text{Bone} \xrightarrow[\text{with } C_6H_6 \text{ or } CS_2]{\text{Washed Powdered}} \text{Bone free from greasy material}$$

$$\Big\downarrow \text{ Burnt in air}$$

$$\underset{\text{(kept in water)}}{\underset{\text{(white)}}{P}} \xleftarrow[C \text{ and } S_iO_2 \text{ in an electrical furnace at } 1200°\text{-}1500°\text{C}]{\text{Mixed with}} \text{Bone ash}$$

Purification : Phosphorous, so obtained, contains impurities of carbon etc. It is melted with potassium dichromate and dil. H_2SO_4 whereby the impurities get oxidised and float on the surface of molten phosphorous. The molten liquid is filtered through chamois leather and distilled. It gives pure phosphorous.

Allotropic Forms of Phosphorous : It exists in five allotropic forms i.e., white, yellow, red, scarlet black and violet etc.

Conversion of White to Red Phosphorous and vice-versa :

$$\text{White } P_4 \xrightarrow[\text{presence of coal gas, cooled)}]{260°\text{C, } I_2 \text{ (Catalyst in}} \text{Red } P$$

$$\xleftarrow[550°\text{, heat, cooled}]{}$$

Comparision Between White or Yellow and Red Phosphorus :

Properties	*White or yellow Phosphorus*	*Red Phosphorus*
1. Colour	Pale yellow	Red solid
2. Smell	Garlic smell	No smell
3. Density	1·8	2·2
4. Melting point (M.P.)	44°C	500-600°C
5. Ignition temperature	30°C	250°C
6. Solubility in CS_2	Soluble	Insoluble
7. In Air	It shows phosphorescence, $P_4+3O_2=2P_2O_3$ $P_4+5O_2=2P_2O_5$	It does not emit light.
8. Action of air	It gets oxidised at ordinary temp. $P_4+5O_2\rightarrow 2P_2O_5$	It is also oxidised by heating (P_2O_5).
9. Action of alkalies (*NaOH*, *KOH* etc.)	It gives Phosphine (PH_3) $P_4+3MOH+3H_2O$ $\rightarrow 3MH_2PO_2+PH_3$ ($M=Na, K$)	×
10. Action of Halogens (Cl_2, Br_2, I_2 etc.)	It reacts with halogens readily giving PX_3 or PX_5 ($X=Cl, Br, I$) $P_4+10Cl_2=4PCl_5$ $P_4+6Cl_2=4PCl_3$	It reacts on heating.
11. Action of Sulphur	It forms sulphide $P_2+6S=2P_2S_3$	It reacts only on heating.
12. Physiological action	Its vapour is poisonous	Its vapour is non poisonous.

Note : From the above reactions, it is clear that white phosphorus is more reactive than red phosphorus. Hence it is kept in water. Since white (P_4) phosphorus is a covalent molecule, it is soluble in covalent solvent such as Benzene, CS_2 or Kerosene oil. Therefore, it is not kept in Kerosene oil.

Uses : Most of the white phosphorus is converted, to the red form. Red phosphorus is used in match industry. The match sticks contain Sb_2S_3 along with an oxidant like PbO_2, $KClO_3$ or K_2CrO_4. The two sides of the match box carry a layer of gum, an abrasive (e.g., powdered glass) and red phosphorus. On striking the match stick against the side of the match box there is a momentary flash which lights the match stick head.

Red phosphorus is also used in (a) the preparation of *HBr*, *HI*, (b) making incendiary bombs. White phosphorus is used in the preparation of phosphine (PH_3).

Formula of Phosphorus : White phosphorous has the molecular formula P_4 both in solid and vapour states at moderate temperatures. The four atoms present in the molecule are arranged at the corners of a tetrahedron (Fig. 8.14). At higher temperature (above 600°C), however, dissociation to diatomic molecules, P_2 occurs.

$$P_4 \rightleftharpoons 2P_2$$

The structure of red phosphorus has not yet been completely determined, but there is evidence that it is polymeric and consists of chains of P_4 tetrahedra linked together possibly in the manner as shown in Fig. 8.15. As compared with white phosphorous, red phosphorus is less reactive, less volatile and less soluble especially in non-polar solvents, because of its highly polymerised structure.

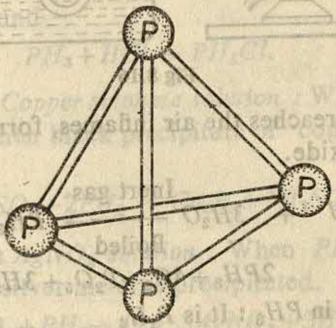


Fig. 8.14. Structure of white phosphorus

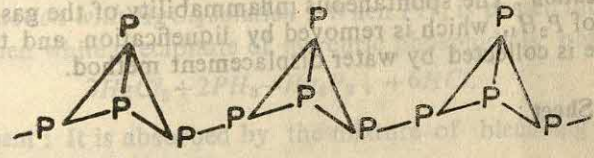


Fig. 8.15. Structure of red phosphorus

8.11. Phosphine

Molecular Formula—PH_3 Molecular Weight—34

Laboratory Method : It is prepared in the laboratory by heating white or yellow phosphorus with caustic soda or caustic potash solution in inert atmosphere

White phosphorous and solution of caustic soda (or caustic potash) are taken into the round bottom flask which is fitted with

COMPARISON OF PH_3 AND NH_3

Terms	Ammonia (NH_3)	Phosphine (PH_3)
1. Smell	Pungent	Rotten fish
2. Litmus	It turns red litmus blue.	It has no effect on litmus.
3. Reaction with Cl_2	It forms NCl_3 only with Cl_2.	It forms PCl_3 and PCl_5 both with chlorine.
4. Reaction with $CuSO_4$ soln.	It gives deep blue solution of $[Cu(NH_3)_4]SO_4$ with $CuSO_4$ solution.	It gives black precipitate Cu_3P_2
5. Reaction with $AgNO_3$ soln.	No Change	It gives white precipitate of Ag_3P with $AgNO_3$ solution

8.12. Phosphorus Trioxide (P_4O_6)

(Phosphorus oxide or Phosphorus anhydride)

Preparation :

It is prepared by heating white phosphorus in a limited supply of air. Some phosphorus pentoxide is also produced. Small pieces of white phosphorus are introduced in a bent tube connected to a Liebig's condenser and a U-tube, The tube is heated while a slow current is being passed from one side by means of a suction pump.

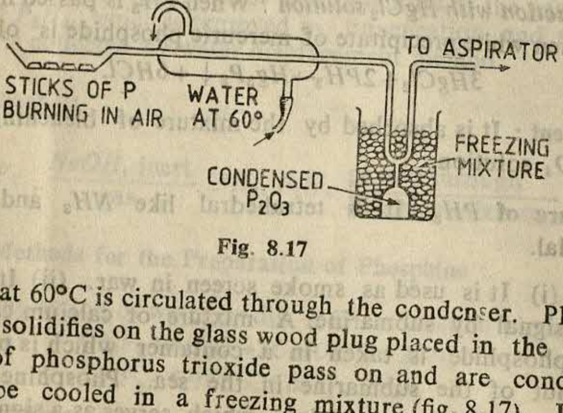


Fig. 8.17

Water at 60°C is circulated through the condenser. Phosphorus pentoxide solidifies on the glass wood plug placed in the way while vapours of phosphorus trioxide pass on and are condensed in the U-tube cooled in a freezing mixture (fig. 8.17). It can be purified by repeated crystallisation from carbon disulphide and exposure to light.

Physical Properties :

(a) It is a white crystalline wax-like solid and has a garlic odour. (b) It is poisonous in nature. (c) It melts at 22·5°C and boils at 173°C.

Chemical Properties :

(a) *Stability :* When it is heated in absence of air to about 400°C, it decomposes to give phosphorus dioxide.

$$4P_4O_6 \rightarrow 6P_2O_4 + P_4$$

(b) *Reaction with oxygen :* It is readily oxidised to P_2O_5 in air or oxygen.

$$P_4O_6 + 2O_2 \rightarrow P_4O_{10}$$

(c) *Reaction with water :* It produces phosphorus acid with cold water. With hot water the reaction is violent and phosphoric acid and phosphina are produced.

$$P_4O_6 + 6H_2O \rightarrow \underset{\text{phosphorus acid}}{4H_3PO_3}$$

$$P_4O_6 + 6H_2O \rightarrow \underset{\text{phosphoric acid}}{3H_3PO_4} + PH_3$$

(b) *Reaction with chlorine :* It burns spontaneously in chlorine to produce oxy-chlorides of phosphorus.

$$P_4O_6 + 4Cl_2 \rightarrow \underset{\text{phospborus oxychloride}}{2POCl_3} + \underset{\text{Metaphosphorous chloride}}{2PO_2Cl}$$

Uses : In the preparation of phosphites.

8.13. Phosphorus Pentoxide (P_4O_{10}, P_2O_5).

(Phosphoric anhydride)

Preparation : It is prepared by burning phosphorus in excess of dry air or oxygen. The white clouds of phosphorus pentoxide settle down to a soft white powder. Some lower oxide is also produced and is converted into the pentoxide by heating the product in a current of dry ozonised oxygen or air. It is further purified by subliming in a current of dry air.

Physical Properties :

(a) It is a white hygroscopic powder. It is odourless when pure. The garlic odour of the impure sample is due to the presence of phosphorus trioxide. (b) It sublimes when heated to 250°C.

Chemical Properties :

(a) *Reaction with Water or Acid charactor :* It reacts with cold water to form metaphosphoric and orthophosphoric acids respectively :

$$P_2O_5+H_2O \rightarrow 2HPO_3 \text{ (Cold water)}$$
$$P_2O_5+3H_2O \rightarrow 2H_3PO_4 \text{ (Hot water)}$$

(b) *As Dehydrating Agent :* It has a great affinity for water and can remove the elements of water from a number of inorganic and organic compounds such as sulphuric acid, nitric acid, alcohol etc.

$$H_2SO_4+P_2O_5 \rightarrow SO_3+2HPO_3$$
$$(2H_2SO_4+P_4O_{10} \rightarrow 2SO_3+4HPO_3)$$
$$2HNO_3+P_2O_5 \rightarrow N_2O_5+2HPO_3$$
$$C_2H_5OH+P_2O_5 \rightarrow C_2H_4+2HPO_3$$
$$\underset{\text{Acetamide}}{CH_3CONH_2}+P_2O_5 \rightarrow CH_3CN+2HPO_3$$

(c) *As Desiccating Agent :* It acts as a desiccating agent for acidic gases.

$$\text{Moist } Cl_2+P_2O_5 \rightarrow \text{Dry } Cl_2 + \boxed{\text{Moisture}+P_2O_5}$$

(d) *With carbon :* It forms carbon monoxide.

$$5CO+P_2O_5 \rightarrow 5CO+2P.$$

Uses :

(i) As a desiccating or drying agent.

(ii) For preparing phosphoric acid.

(iii) As a reagent in organic chemistry.

8.15 Phosphorus Trichloride (PCl)

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(iii) As a reagen

8.15. Phosphorus Trichloride (PCl_3)

Preparation :

It is prepared by heating white phosphorus in a current of dry chlorine :

$$P_4 + 6Cl_2 \rightarrow 4PCl_3$$

The heating is done in a retort on a water bath; phosphorus trichloride distills over and is collected in a receiver cooled in a freezing mixture.

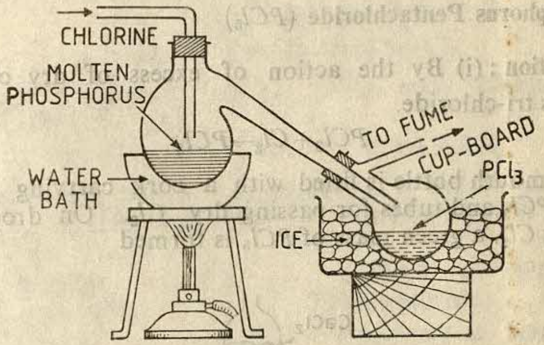


Fig. 8.18

Purification : It is purified redistillation over white phosphorus when phosphorus pentachloride present as an impurity is converted into the trichloride.

Physical Properties :

(a) It is a colourless liquid with pungent odour.
(b) Its boiling point and melting point are 76 and 112°C respectively.

Chemical Properties :

(a) *Reaction with water :* It fumes strongly in moist air. It reacts with water readily to produce phosphorus acid

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

(b) *Reaction with chlorine :* It reacts with dry chlorine to give phosphorus pentachloride.

$$PCl_3 + Cl_2 \rightarrow PCl_5$$

(c) *Reaction with oxygen :* It reacts with dry oxygen slowly to form phosphorus oxychloride.

$$2PCl_3 + O_2 \rightarrow 2POCl_3$$

(d) *Reaction with organic compounds :* It reacts with all organic compounds containing hydroxyl ($-OH$) group, replacing it by a chlorine atom.

$$\underset{\text{Ethyl alcohol}}{3C_2H_5OH} + PCl_3 \rightarrow \underset{\text{Ethyl chloride}}{3C_2H_5Cl} + H_3PO_3$$

$$\underset{\text{Acetic acid}}{3CH_3COOH} + PCl_3 \rightarrow \underset{\text{Acetyl chloride}}{3CH_3COCl} + H_3PO_3$$

Uses : For replacing the hydroxyl group of alcohols, acids etc. by chlorine.

8.16. Phosphorus Pentachloride (PCl_5)

Preparation : (i) By the action of excess of dry chlorine on phosphorus tri-chloride.

$$PCl_3 + Cl_2 \rightarrow PCl_5$$

A wide mouth bottle is fitted with a cork carrying a dropping funnel for PCl_3 and tubes for passing dry Cl_2. On dropping PCl_3 and passing Cl_2, a green mass of PCl_5 is formed

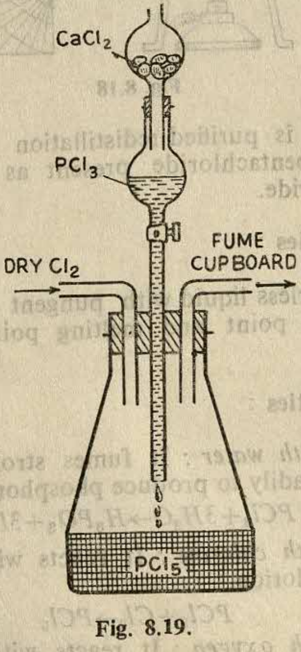


Fig. 8.19.

(ii) By burning phosphorus in excess of chlorine.

$$2P + 5Cl_2 \rightarrow 2PCl_5$$

Properties :

Physical : (a) It is a colourless solid. It turns slightly yellow on standing due to its decomposition into chlorine and phosphorus trichloride. It has a pungent odour.

(b) It sublimes at 100°C. Under pressure, it melts at 148°C.

Chemical : (i) *Action of Heat* : It dissociates to give PCl_3 and Cl_2

$$PCl_5 \rightarrow PCl_3 + Cl_2$$

(ii) *Action of Water* : It reacts readily forming phosphorus oxychloride and phosphoric acid.

$$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$$

$$PCl_5 + 3H_2O \rightarrow H_3PO_4 + 3HCl$$

(iii) *Action of Sulphuric acid* : It reacts with sulphuric acid to form chloro sulphonic acid

$$H_2SO_4 + PCl_5 \rightarrow ClSO_3H + HCl + POCl_3$$

(iv) *Action with Organic Compounds* : It reacts with organic compounds containing hydroxyl ($-OH$) group which is replaced by a chlorine atom.

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + PCl_5 \rightarrow \underset{\text{Ethyl chloride}}{C_2H_5Cl} + POCl_3$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + PCl_5 \rightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + POCl_3 + HCl$$

Uses : It is used in organic chemistry for replacing the hydroxyl group of alcohols, acids etc. by chlorine.

SOME MORE IMPORTANT COMPOUNDS OF PHOSPHORUS

8.17. Sodium Hexa Metaphosphate (Calgon)

$$Na_2[Na_4\,(PO_3)_6]$$

Preparation : It is prepared by burning microcosmic salt $NaNH_4HPO_4, 4H_2O$ or monosodium phosphosphate NaH_2PO_4 and rapidly cooling the fused mass

It is readily soluble in water and forms double salts containing calcium.

$$Na_2[Na_4(PO_3)_6] + 2CaCl_2 \rightarrow Na_2[Ca_2(PO_3)_6] + 4NaCl$$

Even the insoluble calcium salts like carbonate, oxalate, sulphate get dissolved in it.

Uses : (a) As water softener.

(b) In removing crust of insoluble calcium salts from boilers.

(c) In cleaning sinks and dishes.

8.19. Microcosmic salt : (Sod. Amm. Hydrogen Phosphate)

$$NaNH_4.HPO_4$$

Preparation : By dissolving ammonium chloride and disodium hydrogen phosphate in molecular proportions in hot water.

$$Na_2HPO_4+NH_4Cl \rightarrow NaNH_4HPO_4+NaCl$$

On cooling, the crystals of microcosmic salt separate out which are separated by filtration.

Properties : (a) *It is colourless* crystalline solid, soluble in water.

(b) *Action of heat :* When heated NH_3 is given off and glassy mass of sodium metaphosphate is left behind.

$$NaNH_4HPO_4 \rightarrow \underset{\text{Sod. metaphosphate}}{NaPO_3} + NH_3 + H_2O$$

Uses : It is used in the test of silicates and certain basic radicals through microcosmic salt head test.

TYPICAL QUESTIONS WITH ANSWERS

1. *Why does nitrogen differ from the other elements of its group ?*

Ans. Nitrogen is the first element of VA group. It differs from the other members of this group due to the following characteristics :

(a) Small size, (b) high electronegativity, (c) non-availability of, *d*-orbital in valence shell.

2. *Compounds A and B combine to form only one compound C which on heating with NaOH gives back A. Name each compound and give reactions*

Ans. Compound A is ammonia and B may be HCl, HNO_3 or H_2SO_4. Ammonia forms NH_4Cl, NH_4NO_3 and $(NH_4)_2SO_4$ with these acids. These compounds on heating with $NaOH$ give back NH_3 (A).

$$NH_3+HCl \rightarrow NH_4Cl$$
$$NH_3+HNO_3 \rightarrow NH_4NO_3$$
$$\underset{(A)}{2NH_3}+\underset{(B)}{H_2SO_4} \rightarrow \underset{(C)}{(NH_4)_2SO_4}$$
$$(NH_4)_2SO_4+2NaOH \rightarrow 2NH_3+Na_2SO_4+2H_2O.$$

3. *Why ammonium sulphate should not be used in excess as a fertiliser ?*

Ans. The excess of ammonium sulphate makes the soil acidic. Hence it should not be used in excess as a fertiliser.

4. *Why is ammonia desiccated by quick lime, not by* (a) P_2O_5, (b) H_2SO_4 *and* (c) $CaCl_2$ *?*
[Roorkee Entrance, 1983, B.I.T. Meshra '84]

Ans. Ammonia is a base and CaO is basic. Hence both do not react together. In case of P_2O_5, since it is acidic, it reacts to form ammonium phosphate.

$$6NH_3+P_2O_5+3H_2O \rightarrow 2(NH_4)_3PO_4$$

Similarly ammonia reacts with H_2SO_4. and $CaCl_2$. Therefore, they are not used as desiccating agents for NH_3.

$$2NH_3+H_2SO_4 \rightarrow (NH_4)_2SO_4$$
$$8NH_3+CaCl_2 \rightarrow CaCl_2.8NH_3$$

5. *NH_3 is soluble in water but PH_3 is insoluble in water. Explain.*
[CEET 1982]

Ans. NH_3 contains hydrogen bond and it is polar covalent. Hence it is soluble in water. But PH_3 contains no hydrogen bond and it is pure covalent. Hence it is insoluble in water.

6. *NH_3 has higher b.p. than PH_3. Explain.* **[B.I.T. Meshra 1982]**

Ans. NH_3 contains hydrogen bond and PH_3 has got no hydrogen bond. The compound containing hydrogen bond has high b. p. Hence b. p. of NH_3 is greater than that of PH_3.

7. *NCl_3 on hydrolysis gives NH_3 but PCl_3 on hydrolysis gives H_3PO_3. Explain.*

Ans. NCl_3 has a lone pair of electron on '*N*' and it can act as donor only i.e., $:NCl_3$. PCl_3 has lone pair of electron ($:PCl_3$) and it has also empty '*d*' orbital and so PCl_3 can act as donor and acceptor both, more as acceptor because it can increase its covalency greater than 4.

$$:NCl_3+3H_2O \rightarrow NH_3+3OH^-+3Cl^{-1}$$

Nitrogen acts as donor.

$:PCl_3$ acts as acceptor due to its d-orbital.

$$PCl_3+3H_2O \rightarrow H_3PO_3+3HCl$$

8. *Nitrogen forms NCl_3 but phosphorus forms PCl_3 and PCl_5. Why ?*
[P. U. 1980]

Ans. Phosphorus uses the *d*-orbital to extend its covalency but nitrogen does not have *d*-orbital.

9. *Nitrogen exists as N_2 but phosphorus exists as P_4. Explain.*
[CEET 1982]

Ans. In nitrogen (N_2) *N* is stabilised due to π bond formed due to *p p* overlap. The size of *P* is larger than that of *N* and as such *p-p* overlap is not effective and so P is not stabilised as P_2. In solid state P is stabilised as P_4.

10. *White phosphosphorus (P_4) is kept in water, not in organic solvent. Explain.*

Ans. P_4 is a covalent molecule and water is a polar solvent. Hence P_4 is insoluble in water. Since P_4 is covalent molecule, it is soluble in organic solvent (non-polar solvent). Hence it is not kept in organic solvent.

QUESTIONS

Long Type Question :

1. Describe the manufacture of nitric acid from air. Describe three experiments to illustrate the oxidising property of nitric acid. **[P.U. 1972]**
2. Describe with a neat diagram how you will convert ammonia to nitric acid. Explain why H_2SO_4 and not HCl is used in the preparation of HNO_3 from $NaNO_3$ in laboratory. **[R.U. 1970 A]**
3. How is nitric converted into ammonia ? **[B.U. 1972 A]**
4. How does HNO_3 react with :

   (a) C, (b) S, (c) P, (d) I_2, (e) Zn, (f) Mg, (g) Sn, (h) $FeSO_4$, (i) HI, (j) H_2S ? **[B. U. 1971 A, '73 A; M. U. '74 A]**
5. Describe with a neat diagram the manufacture of ammonia on a large scale. What happens when ammonia reacts with :

   (a) Cl_2, (b) H_2O, (c) HCl, (d) $CuSO_4$, (f) $FeCl_3$, (g) CuO, (h) $CuSO_4$? Discuss the conditions of the reactions. **[B.U. 1976 S; M.U. '78 A]**
6. Describe the preparation of ammonia with the help of a neat diagram. How is it dried ? Why is it not dried by means of :

   (a) H_2SO_4, (b) P_2O_5, (c) $CaCl_2$? **[B. U. 1976 S]**
7. Describe with a neat diagram the preparation of nitric oxide in a laboratory. How will you distinguish it from O_2 ? **[R. U. 1979 A; P.U. '74 A]**
8. Describe with a neat diagram the manufacture of phosphorus. How does phosphorus react with (a) Cl_2, (b) HNO_3, (c) H_2SO_4 **(P.U. '86)**. (d) $NaCH$, (e) air ? **[P.U. 1974 S]**
9. Describe with the help of a self-explanatory diagram the laboratory method for the preparation of pure phosphine gas. What happens when phosphine reacts with :

   (a) $CuSO_4$, (b) $AgNO_3$, (c) Cl_2, (d) $HgCl_2$, (e) HI ? **[M.U. 1975 A]**
10. Fill up the blank :

    (a) The shape of ammonia molecule is.............
    (b) The shape of NH_4^+ion is...........
    (c) The shape of N_2O is............
    (d) The shape of PCl_3 is............
    (e) The shape of NO_3^- is......... **[I.I.T. 1971 A]**

11. What happens when :
    (a) NH_4Cl is heated strongly ? [I.I.T. 1976]
    (b) A mixture of $(NH_4)_2, SO_4$ and KNO_3 is heated ? [I.I.T. 1973 A]
    (c) NH_4NO_2 is heated ? [I.I.T. 1974 A]
    (d) $NaNO_3$ is heated with $NaOH$ and Zn powder. [I.I.T. 1968]
    (e) AlN reacts with water ? [I.I.T. 1973 A]
    (f) Mg_3N_2 reacts with water ? [I.I.T. 1973 A]
    (g) White P_4 is boiled with a strong solution of sodium hydroxide in an inert atmosphere ? [I.I.T. 1982]
    (h) NH_4OH solution is added to $CuSO_4$ solution ?
    [B.I.E.C. 1984; W.B.B.J.E.E,'83: P.U. '80: Roorkee Ent. '82]

12. Give the structural formula for the following :
    Phosphorus acid (H_3PO_3), Pyrophosphoric acid, $H_4P_2O_7$ [I.I.T. 1980]

13. Compare and contrast the following pair of compounds in regard to their preparation and two important properties.
    (a) NH_3 and PH_3, (b) NCl_3 and PCl_3 [Roorkee Entrance 1981]

14. What happens when :
    (a) NH_4NO_3 is heated ?
    (b) NH_4NO_2 is heated ? [I.I.T. 1980]
    (c) $Pb(NO_3)_3$ is heated ? [Rookee Ent. 1980]
    (d) KNO_3 is heated ?
    (e) HNO_2 is heated ?
    (f) mixture of $(NH_4)_2SO_4$ and $NaNO_2$ is heated ?

15. Discuss the position of nitrogen and phosphorus in the periodic table.

16. How and under what conditions does nitrogen react with the following ? :
    (a) Hydrogen, (b) Oxygen, (c) Calcium Carbide, (d) Magnesium.
    What is the action of water on the product formed in each case ?

17. Justify the position of nitrogen, phosphorus, arsenic, antimony and bismuth in the V-A group of the periodic table. [Roorkee 1975]

18. How is ammonia prepared in the laboratory and on large scale ? Describe its properties and uses. How would you show that ammonia contains nitrogen and hydrogen ?

19. How is ammonia manufactured by Haber's process ? Give the lablled diagram of the plant and describe the necessary conditions. [B.I.E.C. 1983]

20. Describe the preparation of nitrous acid. Nitrous acid behaves sometimes as an oxidising agent. Illustrate with example.

21. Describe the manufacture of nitric acid on a large scale from ammonia. Describe giving equations, the oxidising action of HNO_3 on :
    (i) H_2S (ii) KI and (iii) SO_2. [M.U. 1980]

22. (a) What are the principles involved in (i) Birkeland-Eyde electric arc process and (ii) Ostwald process for the manufacture of Nitric acid ?
    (b) How does Nitric acid react with (i) Sulphur and (ii) iron ?
    [B.I.E.C. 1985]

23. How is nitric acid obtained from ammonia ? What happens when HNO_3 reacts with the following under different conditions ? :
(a) C, (b) S, (c) Zn, (d) Cu.

24. Describe the preparation, properties and uses of nitrous oxide. How would you :
(i) distinguish it from oxygen ?
(ii) from NO_2 ?

25. Name the different hydrides of nitrogen. How will you prepare one of them in the laboratory ? What happens when ammonia reacts with
(a) CuO, (b) Cl_2, (c) $CuSO_4$ solution ?

26. What do you understand by the term fixation of nitrogen ? Give a brief but clear description of the methods employed for bringing atmospheric nitrogen into combination. Why is the importance of nitrogen in industry increasing ?

27. (a) What is the most important source of phosphorus ? How is it prepared on a large scale ? Mention the chief properties and uses of phosphorus.
(b) What happens when yellow phosphorus reacts with (i) caustic soda (ii) H_2SO_4 and (iii) Iodine ? Name the products formed in each case.

28. Describe the preparation of phosphine. Compare and contrast its properties with those of NH_3.

29. Explain the following :

(a) NH_3 is soluble in water but PH_3 is insoluble in water.
(b) Nitrogen is written as N_2 but phosphorus is written as P_4.
(c) HNO_3 is an oxidising agent.
(d) HNO_2 is a reduciag agent.
(e) HNO_3 is an oxidising agent.
(f) NH_3 has higher b. p. than PH_3. [B.I.T. Meshra 1983
(g) N_2 is used in flash-bulb.
(h) NH_3 is used as refrigerant.
(i) PH_3 is used in Holme's signal.
(j) H_3PO_3 is a dibasic acid.
(k) H_3PO_2 is a monobasic acid.
(l) Why sulphate ammonium should not be used in excess as a fertiliser ?
(m) NH_3 acts as reducing agent.

30. What happens when :
(a) HNO_3 reacts with : (i) S, (ii) I_2, (iii) P, (iv) Sn (IIT 1979), (v) Fe, (vi) Mg, (vii) Hg, (viii) Zn, (ix' Cu, (x) HI ? (I.I.T. 1978)
(b) HNO_2 reacts with : (i) Cl_2, (ii) $KMnO_4$, (iii) $SnCl_2$, (iv) $K_2Cr_2O_7$, (v) H_2S ?
(c) NH_3 reacts with : (i) Cl_2, (ii) $FeCl_3$ solution, (iii) CuO, (iv) $CuSO_4$ solution, (v) Hg_2Cl_2, (vi) $AgCl$, (vii) $Al_2(SO_4)_3$, (viii) CO_2 ?

31. Fill up the blank and balance—
(a) $NH_3+Cl_2\rightarrow$.........$+NH_4Cl$
(b) $Zn+HNO_3\rightarrow NH_4NO_3+$.........$+H_2O$

(c) $HNO_2+KI+........\rightarrow I_2+NO...+......$

(d) $PH_3+AgNO_3\rightarrow.........+.........$

(e) $PCl_5+H_2O\rightarrow.........+.........$

(f) $KNO_3+FeSO_4+H_2SO_4$ (conc.)$\rightarrow$ **(I.I.T. 1980)**

(g) $Mg_3N_2+H_2O\rightarrow......$ **(I.I.T. 1980)**

32. How will you bring about the following conversion ?
    - (a) NH_3 to HNO_3 and vice versa.
    - (b) White phoshhorus to PH_3.
    - (c) Bone to (i) white phosphoric (ii) PH_3 (iii) Orthophosphoric acid, (iv) Red phosphorus.
    - (d) White phosphorus to red phosphorus and vice versa, **(BIEC 1985)**

33. Distinguish between the following :
    (Give the name of the reagent)
    - (i) N_2O and O_2,
    - (ii) NH_3 and PH_3,
    - (iii) HNO_2 and HNO_3,
    - (iv) White P_4 and Red P,
    - (v) NO and NO_2,
    - (vi) $NaNO_2$ and $NaNO_3$,
    - (vii) NO and N_2O.

34. (a) Why NH_3 is not desiccated by :
    (i) Conc. H_2SO_4, (ii) $CaCl_2$, (iii) P_2O_5 ?
    - (b) What is ring test fot nitrate ?
    - (c) Why is fresh solution of $FeSO_4$ used in ring test ?

35. Write down the electron dots formula of :
    (i) HNO_3, (ii) HNO_2, (iii) PCl_5, (iv) P, (v) $H_4P_2O_7$, (vi) H_3PO_2, (vii) H_3PO_3, (viii) NH_3, (ix) PH_3.

Short Answer Type :

36. Test tubes A and B contain differently coloured pieces of phosphorus. On adding sodium hydroxide solution to each and heating an offensive smell is produced in A while no gas seems to be evolved in B.
    - (i) What would you observe if CS_2 had been added to A and B instead of sodium hydroxide, without heating the contents ?
    - (ii) Which of the pieces (in A or in B) would catch fire spontaneously on touching with a warm wire ?
    - (iii) Which of the two test tubes contains a poisonous substance ?

37. (i) What is fixation of nitrogen ?
    - (ii) Give two instances of fixation of nitrogen, one in nature and second in industry. Write equations for the reactions involved in one of these.

38. Arrange the hydrides PH_3, AsH_3 and SbH_3 :
    - (i) in the decreasing order of the stability.
    - (ii) in the increasing order of their boiling points.
39. (a) What variety of phosphorus is commonly used in matches.
    - (b) Which phosphorus is kept in water ?
    - (c) Uses of PH_3.
40. Fill in the blanks :
    - (a) When nitrogen is passed over..........., nitroline is formed.
    - (b) Haber's process is a method of.........of atmospheric nitrogen and is used in manufacture of.........
    - (c) Magnesium burns in nitrogen forming.........
    - (d) Red phosphorus and white phosphorus are.........forms of phosphorus.
    - (e) ....phosphorus has very low igintion temperature.
    - (f) The stable allotrope of phosphorus is.........
    - (g) Red phosphorus is......... in carbon disulphide.
41 Why does nitrogen differ from the other elements of its group ?
42. Why are the elements of V-A group known as elements of *p*-block ?
43. How is nitrogen obtained from ammonia ? Give two equations,
44. Give two reactions each in which HNO_2 acts as oxidising and reducing agont.
45. What is aqua regia ? How does it dissolve noble metals ?
46. Give names and formulae of four nitrogenous fertilisers.
47. You are given the element C, H, N, P and O. Name the compounds which satisfy the following conditions :
    - (a) A triatomic gas used as anaesthesia.
    - (b) A tetratomic gas used as refrigerant.
    - (c) Two diatomic oxides which are neutral.
    - (d) Two tetratomic acids which are used as oxidising agent and reducing agent.
    - (e) A white solid which gives N_2O on heating
    - (g) A tetratomic gas used in Holme's signal.
    - (h) A compound in which O.S. of nitrogen is $-\frac{1}{3}$.
    - (i) A pentatomic acid which is an oxidising agent.
    - (j) An organic fertiliser containing C, N, H and O.
48. Match A with B.

A	*B*
(1) Ostwald process,	(a) is a neutral oxide.
(2) Haber's process.	(b) is used in Holme's signal.
(3) NO	(c) is used in manufacture of HNO_3.
(4) HNO_2	(d) is used in manufacture of NH_3.
(5) PH_3	(e) is used in anaesthesia.
(6) N_2O	(f) is used as o. a. and r. a.

49. State whether the following Statement is *True* or *False*.
   - (a) NH_3 has got sp^2 hybridisation.
   - (b) NH_3 is insoluble in water, (c) PH_3 is soluble in water,
   - (d) P_4 is soluble in CS_2.
   - (e) Red phosphorus is used in safety match.
   - (f) PH_3 is used in Holme's signal.
   - (g) H_3PO_3 is a dibasic acid.
   - (h) H_3PO_2 is a monobasic acid.
   - (i) H_3PO_4 is a tribasic acid.
   - (j) N_2O is used in anaesthesia.
   - (k) NO_2 is neutral but NO is acidic.
   - (l) NH_3 has higher b.p. than PH_3,

Select and Write the Correct answers

50. It is recommended that liquor ammonia bottles be opened after cooling them in ice for sometime. This is because liquor ammonia :
   (1) brings tears to the eyes. (2) is a mild explosive. (3) is a corrosive liquid. (4) has a high vapour pressure.

51. Which of the following properties of white phosphorus is shared by red phosphorus ?
   (1) It phosphoresces in air. (2) It reacts with hot aqueous $NaOH$ to give PH_3.
   (3) It dissolves in CS_2. (4) It burns when heated in air.

52. One of the acids listed below is formed from P_2O_3 and the rest are formed from P_2O_5. The acid formed from phosphorus oxide is :
   (1) HPO_3, (2) $H_4P_2O_7$, (3) H_3PO_4, (4) H_3PO_3.

53. Which of the following is a monobasic acid ?
   (1) H_3PO_4, (2) $H_4P_2O_7$, (3) H_3PO_3, (4) H_3PO_2.

54. Which of the following oxides of nitrogen is the anhydride of nitrous acid ?
   (1) NO, (2) N_2O_5, (3) N_2O_3, (4) N_2O_4.

55. Density of N_2 gas prepared from air is slightly greater than that of N_2 prepared by chemical reaction from a compound of N_2 due to the presence of the following in aerial N_2 :
   (1) Argon, (2) CO_2, (3) some N_3, molecule analogous to O_3, (4) greater amount of N_2 molecule derived from 15 isotopes.

56. Action of conc. HNO_3 on metallic tin produces :
   1. stannous nitrate, 2. stannous nitrite, 3. stannic nitrate,
   4. hydrated stannic oxide.

57. H_3PO_3 is :
   (1) a tribasic acid, (2) a dibasic acid, (3) neutral, (4) monobasic acid.

58. Hypophosphorus acid H_3PO_2 is :
   (1) a tribasic acid, (2) a dibasic acid, (3) a monobasic acid,
   (4) not acidic at all.

59. Which of the following oxides is the true acidic anhydride ?
(1) CO, (2) NO, (3) ClO_2, (4) N_2O_5.

60. In modern process phosphorus in manufactured by
(1) heating a mixture of phosphorite mineral with sand and coke in electric furnance. (2) heating calcium phosphate with coke. (3) heating bone ash with coke. (4) heating the phosphate mineral with sand.

61. The ammonia is dried over :
(1) the slaked lime, (2) quick lime, (3) calcium chloride, (4) phosphorus pentoxide.

62. When conc. HNO_3 is heated with P_2O_5 it forms
(1) N_2O, (2) NO, (3) NO_2, (4) N_2O_5.

63. If excess of NH_4OH is added to $CuSO_4$ solution, it forms :
(1) $[Cu(NH_4)_3]SO_4$, (2) $[Cu\ (NH_3)_3]SO_4$, (3) $[Cu(NH_3)_4]SO_4$,
(4) $[Cu(NH_4)_4]SO_4$.

64. Non-combustible hydride is :
(1) PH_3, (2) NH_3, (3) AsH_3, (4) SbH_3.

65. Ammonia can be dried by :
(1) Conc. H_2SO_4, (2) P_2O_5, (3) Anhy, $CaCl_2$. (4) Anhyd. $CuSO_4$, (5) None.

66. Nitrogen is produced by heating :
(1) HNO_3, (2) NH_4Cl, (3) solution of NH_4Cl and $NaNO_2$, (4) NH_4NO_3.

67. Hydride of nitrogen which is acidic is :
(1) NH_3, (2) N_2H_4, (3) N_2H_2, (4) N_3H.

68. Cane sugar reacts with conc. HNO_3 to give :
(1) CO_2 and H_2O, (2) $CO+H_2O$, (3) carbonic acid, (4) oxalic acid.

69. The reddish brown coloured gas formed when nitric oxide is oxidised by air is :
(1) NO_2, (2) N_2O_4, (3) N_2O_5, (4) N_2O.

70. A mixture contains O_2 and N_2 in the ratio of 1 : 4 by weight. Therefore, the ratio of their number of molecules is :
(1) 1:4, (2) 3 : 16, (3) 7 ; 32, (1) 1 : 8,

□ □ □

CHAPTER 9

STUDY OF THE OXYGEN GROUP OF ELEMENTS

(Elements of Group VI A)

9.1. Periodic Discussion

VI group consists of nine elements divided into VI-A and VI-B sub-groups. The family relationships of this group are shown below :

$$
{}_{8}O - {}_{16}S \begin{array}{l} \nearrow {}_{34}Se - {}_{52}Te - {}_{84}Po \ldots\ldots \text{VIA} \\ \searrow {}_{24}Cr - {}_{42}Mo - {}_{74}W - {}_{92}U \ldots\ldots \text{VIB} \end{array}
$$

The typical elements of this group are oxygen and sulphur. Sulphur may be regarded as a *bridge element* of the sub-group A and B because it resembles both selenium and chromium.

The Family characteristics :

The sixth A group of the periodic table consists of the normal elements oxygen., sulphur, selenium, tellurium and polonium. Oxygen and sulphur are the *typical elements* of this group. The first three elements are non-metals. They are referred to as *chalcogens* (ore forming elements) because many common ores of metals are either oxides or sulphides.

The electronic configuration of VI-A group elements ends with $ns^2\ np^4$ grouping (p-block elements) preceded by a completed shell of 2, 8, or 18 electrons. The four p-electrons are arranged in the three 'p' orbitals as $np_x^2 np_y^1 np_z^1$. Thus there are two half-filled 'p' orbitals which are responsible for chemical bonding with other elements. They thus show the properties of normal elements with usual valency of 2 and maximum valency $+6$.

The properties of elements of oxygen family are summarised as follows :

Properties of Elements of Oxygen Family

Element	*Abundance in earths crust* (ppm)	*Atomic number*	*Electronic configuration*	*Ionic radius* (Å)	*B. P.* (K)	*M. P.* (K)	*Density in the solid state* (gm/ cm^{-3})	*Electro-negativity*	*I. P.* kJ $mole^{-1}$	*O. S.*
O	466,000	8	(*He*) $2s^2 2p^4$	1·4	90	55	1·14	3·50	1314	−2
S	520	16	(*Ne*) $3s^2 3p^4$	1·85	718	392*m**	2·07	2·50	1000	−2, +2, +4, +6
Se	0·09	34	(*Ar*) $3d^{10} 4s^2 4p^4$	1·98	958	490*g***	4·79	2·40	941	−2, +2, +4, +6
Te	0·002	52	(*Kr*) $4d^{10} 5s^2 5p^4$	2·21	1263	723	6·25	2·0	869	−2, +2, +4, +6
Po	—	84	(*Xe*) $4f^{14} 5d^{10} 6s^2 6p^4$	—	1235	527	9·4	1·75	—	+2, +4

***_m_ stands for monoclinic.**
****_g_ stands for grey.**

Oxygen with its high electronegativity value tends to complete its octet by gaining two electrons. Thus most metal oxides are ionic and contain O^{-2} ions. Oxygen exhibits the -2 oxidation state. The electronegativities of the other elements are much less. Hence, there is very low probability for them to form dinegative ions. The tendency for the -2 oxidation state diminishes from sulphur downwards. This is reflected in the instability of the hydrides.

Gradation in VI-A groups :

(i) *Non-metallic character*, *ionisation potential* and *electronegativity* decreases with increase of atomic number. Oxygen is. strongest non-metallic, while polonium (*Po*) is marked metallics Density, atomic volume, ionic radius, melting and boiling point increase with increase in atomic number.

(ii) For oxygen the -2 oxidation state alone is predominant (exceptions : H_2O_2, F_2O and F_2O_2). The other elements show additional oxidation states of $+2$, $+4$ and $+6$. This is due to the presence of vacant *d*-orbitals in these elements.

(iii) *Allotropy* : They show allotropy. Oxygen (two non-metallic forms O_2 and O_3), Sulphur (rhombic, monoclinic, plastic etc.), Selenium (red non metallic, and grey metallic), Tellurium (two forms), Polonium (α- and β-forms).

(iv) *Atomicity* : Oxygen is diatomic (gas) while others are polyatomic (solids) as S_8 property of *Catenation*.

(v) *Hydrides* : All elements of this group form volatile hydrides of the type H_2R. The stability of the hydrides diminishes from oxygen to polonium. While water is an odourless liquid, the other hydrides are offensive smelling gases at ordinary temperatures.

All hydrides, except water, are reducing agents and are weakly acidic. The first two members of the group also give hydrides of the type H_2R_2 (H_2O_2 and H_2S_2). H_2O_2 is stable but H_2S_2 is unstable.

(vi) *Oxides and Oxyacids of S, Se* and *Te* form oxides of MO_2 and MO_3 type. They also form similar oxy-acids.

$$H_2SO_3 \quad H_2SeO_3 \quad H_2TeO_3$$
$$H_2SO_4 \quad H_2SeO_4 \quad H_2TeO_4$$

Strength and stability of the acids decrease from sulphur to Tellurium.

(vii) *Halides* : The elements of this group form a variety of halides. *S*, *Se* and *Te* form di, tetra and hexa halides.

S atom	$3s$	$\underbrace{3p}$	$3d$	
Ground	⇅	⇅ ↑ ↑		sp^2
Excited	⇅	↑ ↑ ↑	↑	sp^3d
Further excited	↑	↑ ↑ ↑	↑	sp^3d^2

Sulphur and selenium also form monohalide e.g. S_2Sl_2.

A few typical halides are indicated below—

Halides of Elements of Oxygen Family

Elements	*Fluorides*	*Chlorides*	*Bromides*	*Iodides*
O	F_2O	Cl_2O, ClO_2, Cl_2O_7	Br_3O	I_3O_5
S	S_2F_2, SF_4, SF_6	S_2Cl_2, SCl_2	S_2Br_2	—
Se	Se_2F_2, SeF_4, SeF_6	$Se_2Cl_2, SeCl_4$	$SeBr_2, SeBr_4$	—
Te	TeF_4, TeF_6	$TeCl_2, TeCl_4$	$TeBr_2, TeBr_4$	TeI_4
Po	—	$PoCl_2, PoCl_4$	$PoBr_3, PoBr_4$	PoI_4

Thus we see that there is close resemblance among oxygen sulphur, selenium, tellurium and polonium. Hence their position in the same group of the periodic table is justified.

ANOMALOUS BEHAVIOUR OF OXYGEN

The first members of group show anomalous behaviour and so does oxygen. Thus, while oxygen is a gas the other elements of the group are all solids. Oxygen molecule is diatomic, but the molecules of other elements are polyatomic. Oxygen shows an oxidation state of -2 while the other elements show additional oxidation states also.

COMPARISON BETWEEN OXYGEN AND SULPHUR

Similarity :

(i) Both are non-metals.

(ii) Both belong to VI group of the periodic table and have similar electronic configuration.

$$_8O = \text{at. no. } 8 = 1s^2,\ 2s^2 2p_x^2 p_y^1 p_z^1$$
$$_{16}S = \text{at. no. } 16 = 1s^2,\ 2s^2 2p^6,\ 3s^2 3p_x 2p_y^1 p_z^1.$$

(iii) Both form similar types of compounds.

$$\left.\begin{matrix}CO_2\\SO_2\end{matrix}\right\} \quad \left.\begin{matrix}H_2O\\H_2S\end{matrix}\right\} \quad \left.\begin{matrix}P_2O_5\\P_2S_5\end{matrix}\right\} \quad \left.\begin{matrix}As_2O_3\\As_2S_3\end{matrix}\right\}$$

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH}; \quad \underset{\text{Thioalcohol}}{C_2H_5SH}$$

(iv) Both combine with hydrogen to form hydrides H_2O and H_2S.

(v) Both form oxides of the formula RO_2 e.g. O_3 and SO_2 where O_3 is regarded as oxide of O_2.

Dissimilarity :

(i) *Physical state* : Oxygen is a gas but sulphur is a solid.

(ii) *Occurrence* : Oxygen is more widely distributed in nature than sulphur.

(iii) *Combination with Hydrogen* : Both form different types of compounds.

H_2O......neutral, colourless ,liquid.

H_2S......acidic, colourless, gas, unpleasant smell.

H_2O contains hydrogen bond, but H_2S has got no hydrogen bond.

(iv) *Combustibility* : Oxygen is a suporter of combustion but sulphur is combustible.

(v) *Action of conc.* HNO_3. : Sulphur is oxidised to H_2SO_4.

$$S+6HNO_3 \rightarrow H_2SO_4+6NO_2+2H_2O$$

9.2. Oxygen (O)

Atomic number : 8 *Mass Number* : 16

Electronic configuration $1s^2 2s^2 2p_x^2 p_y^1 p_z^1$

Occurrence : It is the most abundant of all the elements. In the free state, it occurs to the extent of 21% by volume in the atmospheric air. In the combined state, it occurs in water, in vegetable and animal tissues, in almost all rocks and minerals and also in earth's crust.

Methods of Prepations : Laboratory method :

Principle : It is obtained in the laboratory by heating a mixture of potassium chlorate and manganese dioxide in the ratio 4 : 1 in a hard glass test tube.

$$2KClO_3+[MnO_2] \rightarrow 2KCl+3O_2+[MnO_2]$$

Procedure : A mixture of about 20 gm of $KClO_3$ and 5 gm of MnO_2 is cautiously heated in a hard-glass test tube clamped in a horizontal but slightly inclined position (fig. 9.1). The test tube is

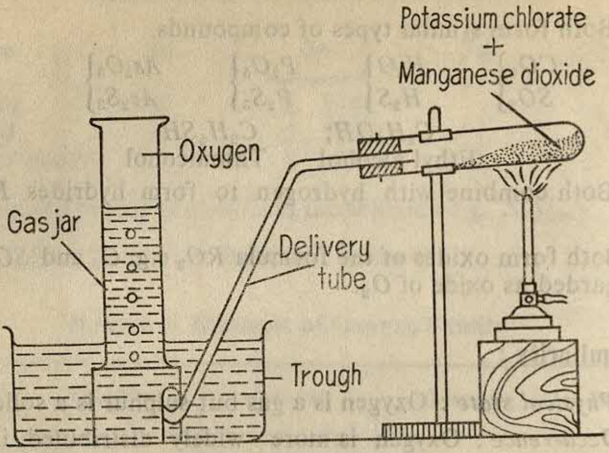


Fig. 9.1.

fitted with a fairly wide delivery tube passing through a cork, with which the test tube is closed. Heating is started with a small flame from the end near the cork and the source of heat is removed whenever the evolution of the gas becomes very rapid. The evolved oxygen is collected in a gas jar by downward displacement of water.

Caution : MnO_2, contaminated with powdered coal, explodes violently when heated with $KClO_3$. It is therefore, advisable to test a little of the above mixture separately, before performing the experiment, in order to be sure that no explosion occurs.

Function of MnO_2 : On heating alone, potassium chlorate melts at 370°C and forms potassium perchlorate and potassium chloride. On raising the temperature to about 630°C, potassium perchlorate loses its oxygen and is converted to KCl.

$$4KClO_3 \rightarrow KCl + 3KClO_4$$
$$KClO_4 \rightarrow KCl + 2O_2$$

If however, a small quantity of MnO_2 is mixed with $KClO_3$, oxygen is given off rapidly at a lower temperature (250°C) and potassium perchlorate is not formed.

$$2KClO_3 + [2MnO_2] \rightarrow 2KMnO_4 + Cl_2 + O_2$$
$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + \text{'}O\text{'}$$
$$2K_2MnO_4 + Cl_2 \rightarrow 2KCl + MnO_2 + O_2$$

Other Methods for the Preparation of Oxygen :

(i) *By heating oxides of Silver and Mercury* : When oxides of silver and mercury are heated, oxygen is produced.

$$2Ag_2O \rightarrow 4Ag + O_2$$
$$2HgO \rightarrow 2Hg + O_2$$

(ii) *By heating Higher Oxides* : When dioxides, peroxides and other higher oxides of metals are heated, oxygen is given out.

$$3MnO_2 \rightarrow Mn_3O_4 + O_2$$
$$3PbO \rightarrow Pb_3O_4 + O_2$$
$$2BaO_2 \rightarrow 2BaO + O_2$$

(iii) *By heating certain salts containing oxygen* : Oxygen can also be prepared by heating certain salts containing oxygen, such as nitrates, chlorates, permanganates etc.

$$2KClO_3 \rightarrow 2KCl+3O_2$$
$$2NaNO_3 \rightarrow 2NaNO_2+O_2$$
$$2Ca(OCl)Cl \rightarrow 2CaCl_2+O_2$$

(iv) *From Sodium Peroxide* : Oxygen gas can also be prepared by the action of water on sodium peroxide.

$$2Na_2O_2+2H_2O \rightarrow 4NaOH+O_2$$

Sodium peroxide is taken in a flat-bottomed flask, fitted with a dropping funnel and a delivery tube. Water is taken in the dropping funnel and added in small amounts to sodium peroxide. Oxygen gas is liberated and collected over water.

Industrial Preparation of Oxygen :

1. *By electrolysis* : Where electricity is cheap, oxygen is manufactured by electrolysis of water containing some amount of an alkali or an acid.

2. *Brine's Process* : It is based upon the fact that at dull red heat barium oxide combines with atmospheric oxygen, forming barium peroxide which decomposes of bright red heat to give the oxygen.

$$2BaO+O_2\xrightarrow{500°C}2BaO_2$$
$$2BaO_2\xrightarrow{800°C}2BaO+O_2$$

Now temperature of barium oxide is kept constant (700°C) and the process is carried out by varying the pressure i.e. it absorbs oxygen at higher pressure and then evolves it at lower pressure.

3. *From liquid air* : The method most commonly used for the manufacture of oxygen from liquid air is due to cloud. It involves following principles :

(i) Cooling is produced by adiabatic expansion of cold compressed gas which causes liquefaction of air.

(ii) On evaporation of liquid air, the more volatile, nitrogen evaporates first leaving oxygen in liquid.

Physical Properties :

(a) Oxygen is a colourless, odourless and tasteless gas.

(b) It is slightly heavier than air.

(c) It is sparingly soluble in water. The small amount of oxygen that the water contains is sufficient for the breathing of all aquatic animals.

(d) It is paramagnetic.

(e) It can be liquefied to a pale blue liquid by cooling under pressure to a very low temperature. On further cooling in liquid hydrogen, it gives a pale blue solid. Its melting point and boiling point are −183°C and −219°C respectively.

Chemical properties :

(a) It is neutral to litmus.

(b) *Supporter of combustion* : It supports combustion and most of the elements form oxides with oxygen.

(c) *Reaction with Non-metals* : Oxygen reacts with a number of non-metals to form oxides.

(i) $P_4+5O_2 \rightarrow P_4O_{10}$ or $2P_2O_5$

(ii) $S+O_2 \xrightarrow{\text{ignited}} SO_2$

$C+O_2 \xrightarrow{\text{ignited}} CO_2$

(iii) $N_2+O_2 \xrightarrow[3000^\circ C]{\text{Electric arc}} 2NO$

(d) *Reaction with Metals* : Oxygen combines with a large number of metals to form metal oxides. Metals such as magnesium, sodium, calcium and aluminium burn brightly when ignited in an atmosphere of oxygen.

$$2Mg+O_2 \rightarrow 2MgO$$
$$4Al+3O_2 \rightarrow 2Al_2O_3$$
$$2Na+O_2 \rightarrow Na_2O_2$$

(e) *Reaction with Nitric Oxide* : It combines with colourless nitric gas at the room temperature to give reddish brown fumes of nitrogen peroxide.

$$2NO+O_2 \rightarrow 2NO_2$$

(f) *Reaction with Ammonia* : Oxygen oxidises ammonia to nitric oxide in the presence of platinum gauze at 800°C (Ostwald's process).

$$4NH_3+5O_2 \rightarrow 4NO+6H_2O$$

(g) *Reaction with Sulphur Dioxide* : Oxygen oxidises SO_2 to SO_3 in the presence of vanadium pentoxide or finely-divided platinum (Contact process).

$$2SO_2+O_2 \underset{Pt}{\overset{450^\circ-500^\circ C}{\rightleftharpoons}} 2SO_3$$

(h) *Conversion to Ozone* : When pure dry oxygen is subjected to a silent electric discharge, it is partially converted to ozone.

$$3O_2 \rightarrow 2O_3$$

(i) *Reaction with Acetylene* : Acetylene gas burns in oxygen with a bright flame to produce a large amount of heat. The flame is known as oxy-acetylene flame and employed for welding purpose.

$$2C_2H_2+5O_2 \rightarrow 4CO_2+2H_2O+312 \text{ kcal/mole}$$

Tests :

(a) A smouldering splinter of wood is rekindled in an atmosphere of oxygen.

(b) It gives reddish brown fumes of nitrogen peroxide with nitric oxide.

(c) It is absorbed by alkaline solution of pyrogallol.

Uses : Oxygen is used :

(a) in oxygen-hydrogen and oxy-acetylene flame.

(b) for the combustion of fuel used in rockets.

(c) for artificial respiration in hospitals in cases of gas poisioning, pneumonia, asthma etc.

(d) Powdered charcoal mixed with liquid oxygen is used as an explosive in coal mining.

OXIDES

When oxygen combines with the elements, then they are called oxides. Example : Magnesium oxide (MgO), Sodium monoxide (Na_2O), and Sulphur dioxide (SO_2).

Methods of Preparation :

(i) *By burning metals or non-metals in oxygen* :

$$2Mg+O_2 \longrightarrow 2MgO$$
$$C+O_2 \longrightarrow CO_2$$

(ii) *By heating metal hydroxides, carbonates, nitrates, sulphates etc.* :

$$Ca(OH)_2 \longrightarrow CaO+H_2O$$
$$CaCO_3 \longrightarrow CaO+CO_2$$
$$2Pb(NO_3)_2 \longrightarrow 2PbO+4NO_2+O_2$$
$$2FeSO_4 \longrightarrow Fe_2O_3+SO_2+SO_3$$

(iii) *By passing steam over red hot metals* :

$$3Fe+4H_2O \longrightarrow Fe_3O_4+4H_2$$

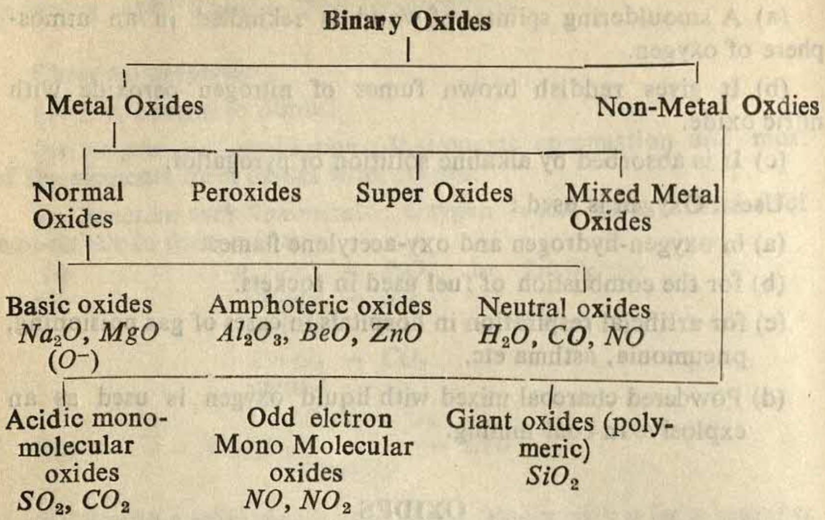
(iv) *By heating Potassium dichromate or Permanganate* :

$$4K_2Cr_2O_7 \longrightarrow 4K_2CrO_4+2Cr_2O_3+3O_2$$
$$2KMnO_4 \longrightarrow K_2MnO_4+MnO_2+O_2$$

(v) *By reducing oxyacids with metals* :

$$Cu+2H_2SO_4 \text{ (conc.)} \longrightarrow CuSO_4+SO_2+2H_2O$$
$$3Cu+8HNO_3 \text{ (dil.)} \longrightarrow 3Cu(NO_3)_2+2NO+4H_2O$$

Classification of Oxides :



Several classifications of binary oxides have been proposed from time to time. The one based on acid/base character and nature of the molecular form is presented above. The salient properties of these binary oxides are given below :

1. **Normal Oxides** : These are the oxides in which the oxidation number of oxygen is the usual -2.

These oxides may be

(a) basic oxides, (b) neutral oxides and (c) amphoteric oxides.

The *basic oxides* are given by those elements whose ionisation potentials are quite low (more electropositive metals) and whose reduction potentials are quite negative. The *alkalies* and the *alkaline earth metals* form such oxides. Aqueous solution of such basic oxides give alkaline reaction due to OH ion. These oxides give salts and H_2O when neutralised with acids.

$$Na_2O+H_2O\rightarrow 2NaOH;\ Na_2O+2HCl\rightarrow 2NaCl+H_2O$$

A few elements, like aluminium, beryllium, zinc give *amphoteric oxide*. These react with both acids and bases.

$$Al_2O_3+6HCl\longrightarrow AlCl_3+3H_2O \text{ . . . . basic character}$$
$$Al_2O_3+2NaOH\longrightarrow 2NaAlO_2+H_2O \text{ . . . . acid character}$$

Neutral oxides are obviously those which show none of the basic or acidic characters, as for example :

H_2O, CO, NO etc.

2. **Peroxides** : These are salts of hydrogen peroxides. In these compounds there is an $[O-O]^{2-}$ single covalent bond in the peroxide ion. On reaction with acids they liberate H_2O_2. Peroxides usually act as oxidants. In presence of acids they also react as reductants

towards they also react as reductants towards strong oxidising agents like $KMnO_4$.

$$Na_2O_2+2HCl \longrightarrow 2NaCl+H_2O_2$$
$$2KI+Na_2O_2+4HCl \longrightarrow I_2+2KCl+2NaCl+2H_2O$$
$$2KMnO_4+5Na_2O_2+8H_2SO_4 \longrightarrow 2MnSO_4+K_2SO_4+5Na_2SO_4 +8H_2O+5O_2$$

3. **Superoxides** : These oxides contain a mononegative ion. The superoxide anion contains an unpaired electron i.e. the ion is an odd-electron ion. Because of the presence of the unpaired electron all superoxides (eg. $Ca(O_2)_2$) are paramagnetic. These are very stong oxidants.

4. **Mixed metal oxides** : They contain two metallic oxides, as for example,

$$Fe_3O_4\ (FeO.Fe_2O_3);\ Co_3O_4\ (CoO.Co_2O_3) \text{ etc.}$$

5. **Non-metal oxides** : (a) Acidic in most cases these oxides are monomeric and *acidic* in nature.

Examples : SO_2, SO_3, CO_2 etc.

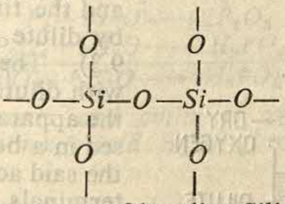
$$CO_2+H_2O—H_2CO_3$$
$$SO_3+H_2O \longrightarrow H_2SO_4$$

Most of these are formed by electronegative non-metals.

(b) *Neutral* : Few non-metal oxides are neutal as for *example* NO, CO, H_2O etc.

(c) *Odd-electron non-metal oxides* : There are few non-metal-oxides which carry odd electrons in their molecule. These are generally monomeric and paramagnetic in nature; examples : NO, NO_2, ClO_2 etc.

(d) *Polymeric non-metal oxides* : One such example is found in silica which is polymeric through oxygen bridging. These oxides have high melting points.



The nature of bonding Silica

93. OZONE

(The active allotrope of Oxygen)

Molecular formula—O_3 Molecular weight—48

Occurrence : Ozone occurs in minute traces (about 1 part per ten million) in air (especially in sea-air) and in somewhat larger quantities in the upper atmosphere. It is also formed in the neighbourhood of frictional electrical machines. Electrolytically prepared oxygen also contains some ozone.

Preparation : Pure ozone is very difficult to prepare. A mixture of ozone with air or oxygen is generally prepared by the action of *silent electric discharge* on air oxygen.

$$3O_2 \rightleftharpoons 2O_3$$

Two types of apparatus viz. the **Siemen's ozoniser** or **Brodie's ozoniser** are generally used for the preparation of ozone in the laboratory.

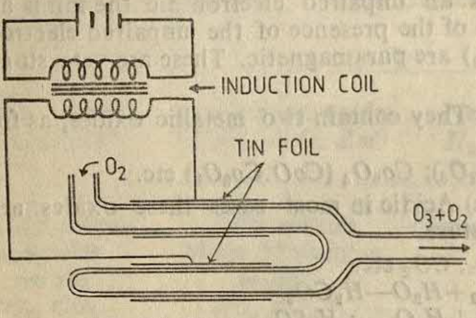


Fig. 9.2. Siemen's ozoniser

(i) Siemen's Ozoniser : This is made up of two co-axial glass tubes fused with each other at one end as shown in fig. 9.2. The inside of the inner tube and the outside of the outer tube are covered with tin-foils. A current of dry and pure oxygen or air is passed through the space between the two tubes and is subjected to *silent electric discharges* by connecting the tin-foils to an induction coil. About 10% of oxygen is converted to ozone and the mixture coming out of the apparatus is ozonised oxygen or ozonised air, according to the gas that was used for the preparation.

(ii) Brodie's Ozoniser : This is almost similar in construction to the Siemen's ozoniser, except that the outlet of the products is bent in the form of a 'U' and the tin-foils are replaced by dilute sulphuric acid (fig. 9.3). The inner tube is filled with dilute sulphuric acid and the apparatus is partly immersed in a beaker containing also the said acid. Wires from the terminals of an induction coil are immersed in the liquids and the current is switched on, while a slow stream of pure and dry oxygen (or air) is passed through the annular space of the apparatus. Ozonised oxygen (or ozonised air) escapes through the outlet tube. The concentration of ozone in the product is about 10%.

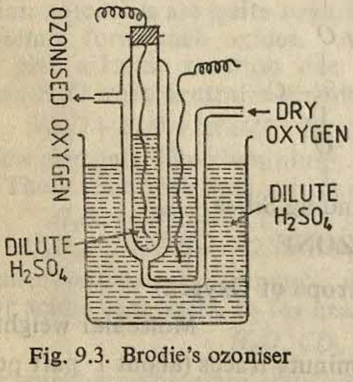


Fig. 9.3. Brodie's ozoniser

Pure ozone may be obtained by cooling ozonised oxygen in liquid air and subjecting the condensed deep blue liquid to fractional evaporation. Liquid oxygen evaporates first, leaving behind less volatile liquid ozone, which may be evaporated and collected subsequently.

Properties of ozone : *Physical properties* : Ozone is a blue gas with a fishy odour. It can be condensed at −112·4°C to a deep blue explosive liquid. It is slightly solube in water but is highly soluble in certain oils like turpentine oil, which is used as an absorbent for the gas.

Chemical Properties :

(a) *Stability* : It is an unstable gas. It decomposes slowly at ordinary temperature and rapidly on heating. The decomposition is catalysed by the presence of cupric oxide, MnO_2, platinum black etc.

$$2O_3 \xrightarrow{250°-300°C} 3O_2$$

(*b*) *As an oxidising agent* : It acts as a strong oxidising agent because it readily undergoes decomposition to produce atomic oxygen. Some important reactions where ozone acts as an oxidising agent are discussed below :

$$O_3 \rightarrow O_2 + \text{‘}O\text{’}$$

(i) It oxidises *sulphur to sulphuric acid* in the presence of water :

$$\begin{array}{c} O_3 \longrightarrow O_2 + O\ [\times 3] \\ \underline{S + 3\text{‘}O\text{’} + H_2O \longrightarrow H_2SO_4} \\ S + 3O_3 + H_2O \longrightarrow H_2SO_4 + 3O_2 \end{array}$$

(ii) *Phosphorous is oxidised to phosphoric acid* in the presence of water :

$$\begin{array}{c} O_3 \longrightarrow O_2 + \text{‘}O\text{’}\ [\times 10] \\ P_4 + 10\ \text{‘}O\text{’} \longrightarrow 2P_2O_5 \\ \underline{P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4\ [\times 2]} \\ P_4 + 10O_3 + 6H_2O \longrightarrow 4H_3PO_4 + 10O_2 \end{array}$$

Similarly *arsenic and antimony are oxidised to arsenic acid* (H_3AsO_4) *and antimonic acid* (H_3SbO_4) respectively in the presence of water.

(iii) It oxidises *silver to silver oxide* :

$$\begin{array}{c} O_3 \longrightarrow O_2 + \text{‘}O\text{’} \\ \underline{2Ag + \text{‘}O\text{’} \longrightarrow Ag_2O} \\ 2Ag + O_3 \longrightarrow Ag_2O + O_2 \end{array}$$

(iv) It oxidises moist *iodine to iodic acid* :

$$\begin{array}{c} O_3 \rightarrow O_2 + \text{‘}O\text{’}\ [\times 5] \\ I_2 + 5\ \text{‘}O\text{’} \rightarrow I_2O_5 \\ \underline{I_2O_5 + H_2O \rightarrow 2HIO_3} \\ I_2 + 5O_3 + H_2O \rightarrow 2HIO_3 + 5O_2 \end{array}$$

(v) It oxidises *metal sulphides to metal sulphates.* Thus lead sulphide (black) is oxidised to lead sulphate (white):

$$\begin{array}{c} O_3 \rightarrow O_2 + \text{'}O\text{'}\ [\times 4] \\ PbS + 4\text{'}O\text{'} \rightarrow PbSO_4 \\ \hline PbS + 4O_3 \rightarrow PbSO_4 + 4O_2 \end{array}$$

(vi) It oxidises *potassium iodide to iodine*:

$$\begin{array}{c} O_3 \rightarrow O_2 + \text{'}O\text{'} \\ KI + H_2O \rightarrow KOH + HI\ [\times 2] \\ 2HI + \text{'}O\text{'} \rightarrow H_2O + I_2 \\ \hline 2KI + H_2O + O_3 \rightarrow 2KOH + I_2 + O_2 \end{array}$$

(vii) It oxidises a solution of *potassium manganate green to potassium permanganate* (pink):

$$\begin{array}{c} O_3 \rightarrow O_2 + \text{'}O\text{'} \\ 2K_2MnO_4 + H_2O + \text{'}O\text{'} \rightarrow 2KMnO_4 + 2KOH \\ \hline 2K_2MnO_4 + H_2O + O_3 \rightarrow 2KMnO_4 + 2KOH + O_2 \end{array}$$

(viii) It oxidises a solution *potassium ferrocyanide* to *pot. ferricyanide*:

$$\begin{array}{c} O_3 \rightarrow O_2 + \text{'}O\text{'} \\ 2K_4[Fe(CN)_6] + H_2O + \text{'}O\text{'} \rightarrow 2K_3[Fe(CN)_6] + 2KOH \\ \hline 2K_4[Fe(CN)_6] + H_2O + O_3 \rightarrow 2K_3[Fe(CN)_6] + 2KOH + O_2 \end{array}$$

(ix) It oxidises acidified *stannous chloride to stannic chloride*:

$$3SnCl_2 + 6HCl + O_3 \longrightarrow \underset{\substack{\text{Stannic}\\ \text{chloride}}}{3SnCl_4} + 3H_2O$$

(x) It oxidises *halogen acids to halogens*:

$$\begin{array}{c} O_3 \rightarrow O_2 + \text{'}O\text{'} \\ 2HCl + \text{'}O\text{'} \rightarrow H_2O + Cl_2 \\ \hline 2HCl + O_3 \rightarrow Cl_2 + H_2O + O_2 \end{array}$$

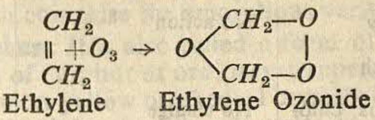
(xi) It oxidises $\underbrace{SO_2 \text{ to } SO_3}$:

$$\begin{array}{c} O_3 \rightarrow O_2 + \text{'}O\text{'} \\ SO_2 + \text{'}O\text{'} \rightarrow SO_3 \\ \hline SO_2 + O_3 \rightarrow SO_3 + O_2 \end{array}$$

(c) *As reducing agent*: When ozone reacts with peroxides such as hydrogen peroxide and barium peroxide, both the reactions undergo reduction with the liberation of oxygen.

$$H_2O_2+O_3 \rightarrow H_2O+2O_2$$
$$BaO_2+O_3 \rightarrow BaO+2O_2$$

(d) *Formation of Ozonised compound* : It reacts with unsaturated organic compounds containing double bonds, such as ethylene, to form addition products called *ozonides.*



(e) *As Bleaching Agent* : Ozone acts as a bleaching agent. The atomic oxygen that it liberates on decomposition oxidises colouring matter to colourless compounds. Thus it can bleach vegatable matter, silk, starch, wax and oils.

Tests : (a) Ozone can be detected by its sharp characteristic smell.

(b) It turns starch iodide paper blue.

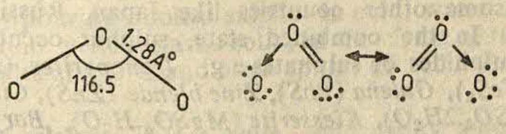
(c) Ozone turns benzidine paper brown and tetramethyl base paper violet.

(d) A clear silver coin is turned black by ozone.

Uses : Ozone is used :

(a) for bleaching silk, ivory, wax and oils, (b) as a germicide for sterilsation for drinking water, (c) in the manufacture of synthetic camphor and artificial silk, (d) in improving the atmosphere of crowded places, such as cinema halls, mines and underground railways.

Structure of Ozone : The three oxygen atoms of ozone are at the apices of an equilateral triangle. The real structure is a resonance hybrid of the structures shown below. It has get sp^2 hydridisation.



By physical methods the angle between $O-O-O$ is 116·5° and $O-O$ bond length is 1·28Å. It has got a resonating structure.

Composition of Ozone : Its composition can be determined by *Sorret's* experiment and *Newth's* experiment.

Comparison between Hydrogen peroxide and Ozone

Tests	*Hydrogen peroxide*	*Ozone*
1. Smell	Smells like nitric acid	It has a fishy smell
2. With mercury	No action	Mercury loses its mobility
3. Reactions with		
(a) Manganous chloride	No change	Turns brown
(b) Benzidine	No change	Turns brown
(c) $KMnO_4$ solution acidified with H_2SO_4	Colour discharged	No action
(d) $K_2Cr_2O_7$ solution acidified with dil. H_2SO_4 + ether	Ether layer turns blue	No action
(e) KI solution + $FeSO_4$ solution	Iodine liberated	Iodine is not liberated
(f) Solution of tetramethyl base (Tetramethyl diamino diphenylmethane)	No change	Violet colour is formed

9.4. SULPHUR

Symbol—S Atomic number—16 Atomic weight—32·06

Electronic configuration $1s^2 2s^2 2p^6 3s^2 3p_x^2 p_y^1 p_z^1$

Occurrence : Sulphur occurs in nature both in the free and the combined states. Free suphur occurs in large quantities in Sicily, (Italy), Louisiana and Texas (U.S.A.) and smaller quantities are available in some other countries like Japan, Russia, Chile and Newzealand. In the combined state, sulphur occurs in ores and minerals as sulphides or sulphates e.g. *Iron pyrites* (FeS_2), *Copper pyrities* ($CuFeS_2$), *Galena* (PbS), *Zinc blende* (ZnS), *Cinnabar* (HgS), *Gypsum* ($CaSO_4.2H_2O$), *Kiesserite* ($MgSO_4.H_2O$), *Barytes* ($BaSO_4$). Many organic matter such as egg, onion, garlic and mustard contain sulphur compounds.

Extraction of Sulphur : It is extracted by (a) Frasch process,
(b) Sicillian process and
(c) Gill process.

Allotropic Forms : Sulphur exists in different allotropic modifications, of these, the crystalline varities consist of (i) *Rhombic* or *Octahedral* form (α-sulphur), (ii) *Monoclinic* or *Prismatic form* (β-sulphur) and two other unstable species viz. (iii) *Tabular form* and (iv) *Pearly* or *Nacreous* form. The other varities are (v) *Plastic sulphur* (γ-sulphur), (vi) *Milk of sulphur* and (vii) *Colloidal sulphur* (δ-sulphur), which comprise the amorphous varities.

Rhombic Sulphur : It is also called α-form of sulphur. It is the most stable form of sulphur at ordinary temperature and is obtained as transparent lemon-yellow octahedral crystals on slow evaporation of solution of roll sulphur in CS_2. It melts at 114·8°C and has a sp. gr. of 2·06. It is highly soluble in CS_2. This form of sulphur is stable up to 95·5°C, above which it changes to the monoclinic variety. Its molecule is composed of 8 atoms which are bound together in a closed ring.

$$S_\alpha \overset{96°C}{\rightleftharpoons} S\beta$$

It has puckered ring structure.

Monoclinic Sulphur : It is formed as transparent needle-shaped crystals when molten sulphur is allowed to cool slowly. It melts at 119°C and has a sp. gr. of 1·96. It is freely soluble in CS_2. This form of sulphur is stable within the narrow temperature range of 95·5°C-119°C. Below 95·5°C, the rhombic sulphur is stable. The change from rhombic to monoclinic form is reversible and takes place exactly at 95·5°C, which is called their *transition temperature*. This variety also forms S_8- molecules.

Preparation of Monoclinic sulphur : Monoclinc sulphur is generally prepared in the following way : Some quantity of roll sulphur is taken in a porcelain basin and is completely melted by slow heating. The molten mass is allowed to cool in air when a crust is formed on the surface of the liquid. After some time the crusted surface is pierced by a glass rod to make a hole, through which the molten sulphur, still remaining in the basin, is decanted off. The crust is then removed and the long needle-shaped, transparent crystals of monoclinic sulphur are collected from the sides of the basin.

Plastic sulphur : This is an amorphous form of sulphur and is obtained by pouring molten sulphur in cold water in a thin stream. A transparent yellow elastic solid, in the form of threads, is obtained. It melts at 120°C and has a sp. gr. of 1·92. It is insoluble in CS_2.

Milk of sulphur : This is white, amorphous sulphur, soluble in CS_2. It is formed by boiling powdered roll sulphur with milk of lime and acidifying the resultant clear yellow liquid with dilute HCl solution.

$$12S+3Ca(OH)_2 \rightarrow \underset{\text{Cal. Pentasulphide}}{2CaS_5}+CaS_2O_3+3H_2O$$

$$2CaS_5+CaS_2O_3+6HCl \rightarrow 3CaCl_2+12S+3H_2O$$

Colloidal Sulphur : A milky colloidal suspension of sulphur is obtained on acidification of a solution of sodium thiosulphate, or on passing hydrogen sulphide gas into a solution of sulphur dioxide in water. Some forms of colloidal sulphur are soluble in CS_2 while some other forms insoluble.

$$2H_2S+SO_2\rightarrow 3S+2H_2O$$
$$H_2S+2HNO_3\rightarrow 2NO_2+2H_2O+\underset{\text{colloidal sulphur}}{S}$$

Properties of Sulphur :

Physical Properties : Sulphur is a yellow, brittle solid, melting at about 113°C and boiling at 444·6°C. It is a very poor conductor of heat and electricity. It is insoluble in water, but is highly soluble in CS_2.

When roll sulphur is heated from the room temperature upwards, it changes to the monoclinic form above 96°C and remain in this form till it melts at about 113°C, on increasing the temperature the melt turns into a pale coloured mobile liquid at about 160°C and this turns to an almost solid viscous mass at about 230°C. At about 300°C, the viscous mass again changes to a mobile liquid which boils at 444·6°C.

Sulphur exhibits variable valencies in its compounds. Thus in hydride (H_2S) its valency is 2 units, whereas in sulphur dioxide (SO_2) and sulphur trioxide (and in the corresponding oxy-acids and salts) the valency is 4 and 6 units respectively.

Chemical Properties :

(a) *Reaction with non-metals* : (i) Sulphur burns with blue flame in oxygen or air producing SO_2. A small quantity of SO_3 is formed.

$$S+O_2\rightarrow SO_2$$
$$2SO_2+O_2\rightleftharpoons 2SO_3$$

(ii) *With hydrogen* : Boiling sulphur forms H_2S.

$$H_2+S\rightarrow H_2S$$

(iii) *With Cl_2* : Boiling sulphur forms sulphur-monochloride.

$$2S+Cl_2\rightarrow S_2Cl_2$$

(iv) *With carbon* : When sulphur vapour are passed over red hot *coke* carbon disulphide is obtained.

$$C+2S\rightarrow CS_2$$

(v) *With phosphorus* : It forms phosphorous pentasulphide.

$$2P+5S\rightarrow P_2S_5$$

(b) *Reaction with metals* : It combines with most of the metals such as iron, copper, lead, zinc and mercury on heating to form sulphides.

$$Fe+S\rightarrow FeS$$
$$Zn+S\rightarrow ZnS$$

(c) *As reducing agent* : (i) It reduces conc. H_2SO_4 to SO_2 on heating.

$$H_2SO_4 \rightarrow SO_2 + H_2O + \text{'}O\text{'} \ [\times 2]$$
$$\underline{S + 2\text{'}O\text{'} \rightarrow SO_2}$$
$$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$$

(ii) Conc. HNO_3 is reduced to NO_2.

$$2HNO_3 \rightarrow NO_2 + H_2O + \text{'}O\text{'} \ [\times 2]$$
$$\underline{S + 2\text{'}O\text{'} \rightarrow SO_2}$$
$$S + 4HNO_3 \rightarrow 4NO_2 + SO_2 + 2H_2O$$

(d) *Reaction with alkalies* : When sulphur is boiled with alkalies solution then a mixture of a sulphide and thiosulphate is produced.

$$4S + 6KOH \rightarrow \underset{\substack{\text{Pot.}\\ \text{sulphide}}}{2K_2S} + \underset{\substack{\text{Pot. thio-}\\ \text{sulphate}}}{K_2S_2O_3} + 3H_2O$$

Similarly $4S + 3K_2CO_3 \rightarrow 2K_2S + K_2S_2O_3 + 3CO_2$

Uses : Sulphur is used in the preparation of SO_2 (for sulphuric acid manufacture), calcium bisulphite (for paper industry), carbon disulphide, sulphur chloride, sodium thiosulphate etc. It is also used as an ingredient for making gun-powder, matches, fireworks, ultramarine (blue) and dyes, as well as for the vulcanization of rubber. It finds application in medicine (colloidal sulphur, milk of sulphur, liver of sulphur) and as a fungicide.

Tests : (i) Yellow solid, insoluble in water but highly soluble in CS_2. (ii) It burns in air with a pale blue flame, giving choking smell of SO_2. (iii) The gas obtained by burning sulphur turns (a) lime water milky, (b) orange coloured acidified solution of potassium dichromate green and (c) pink coloured acidified potassium permanganate solution colourless.

Comparison between rhombic, monoclinic and plastic sulphur

Property	Rhombic sulphur	Monoclinic sulphur	Plastic sulphur
1. Appearance	Pale yellow	Colourless	Yellow-brown
2. Nature	Soild, Crystalline	Solid, Crystalline	Solid, amorphous
3. Shape of crystals	Orthorhombic	Monoclinic (Prismatic)	
4. Density	2·06	1·96	1·92
5. Solubility in CS_2	Soluble	Soluble	Not soluble
5. Melting point	112·8°C	119°C	120°C

To prove that the different forms of sulphur are the allotropic modifications of the same element

Although the various forms of sulphur possess different physical properties but they are chemically identical and hence, they are just the different forms of the same element. Two proofs may be adduced in support of this statement.

(i) The various forms of sulphur are interconvertible. When any form is vaporised and the vapours are cooled on contact with a cold surface, the product is found to be the same in all cases.

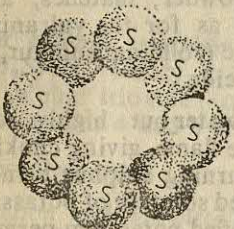
(ii) If equal weights of the different forms of sulphur are separately treated in the same manner, the same product (with same weight) is formed in each case.

If equal weights of all the forms are burnt in air separately, in each case, the product is sulphur dioxide, and if the weight of the product is measured, it will be found to be the same in each case.

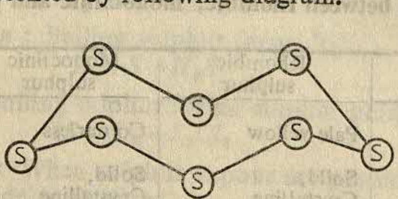
Structure of sulphur : α-sulphur is stable at ordinary temperature. At 96°C it is converted to β-sulphur. Again it is converted to α-sulphur below 96°C.

$$S_\alpha \overset{96°C}{\rightleftharpoons} S_\beta.$$

This temperature is called *transition temperature* of sulphur. It is found that α-sulphur molecule is S_8. Eight atoms of sulphur form puckered ring.



S_8 can be represented by following diagram.



COMPOUNDS OF SULPHUR

9.5. Hydrogen Sulphide (Sulphurated Hydrogen)

Mol. Formula—H_2S Mol. wt. = 34

Laboratory Method : In laboratory it is generally prepared by the action of dil. sulphuric acid or dilute hydrochloric acid on iron sulphide or iron pyrite.

(a) $FeS+2HCl \rightarrow FeCl_2+H_2S$

$FeS+H_2SO_4 \rightarrow FeSO_4+H_2S$

(b) $FeS_2+2HCl \rightarrow FeCl_2+H_2S+S$

Iron pyrite

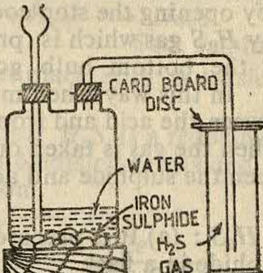


Fig. 9.4.

In the laboratory it is prepared in Woulf's bottle as shown in fig. 9.4 But for qualitative analysis, it is prepared in Kipp's apparatus, as shown in fig. 9.5.

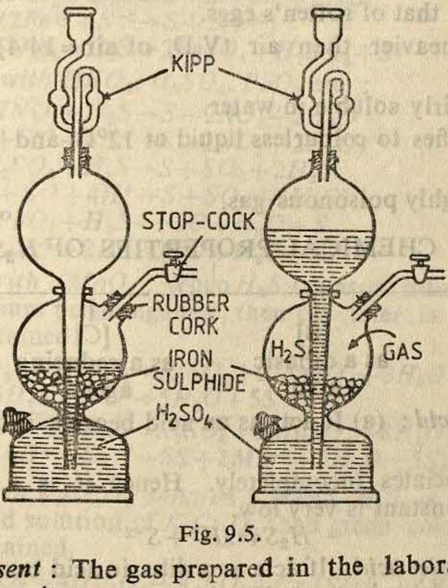


Fig. 9.5.

Impurity present : The gas prepared in the laboratory contains Hydrogen as impurity.

Iron is present as impurity in iron sulphide.

Description of Kipp's apparatus : It consists of two parts. The lower part contains two bulbs while the upper bulb having a long stem which passes through the two bulbs of the base and reaches the bottom of the apparatus. The middle bulb contains the stop cock '*S*' for the passing of gas. The apparatus is emptied through stopper which is fitted in the bottom.

Iron sulphide is placed in the middle bulb and acid is poured from the top bulb so that it covers the iron sulphide when the stop-cock is opened. The reaction between acid and iron sulphide is allowed to take place by opening the stop-cock. The acid is pushed into the bottom bulb by H_2S gas which is produced in the middle bulb. The acid from the bottom bulb goes up into the top bulb through the long stem. In this way when middle bulb is filled with the gas the contact between the acid and iron sulphide is broken and the reaction stops. When the gas is taken out by opening the stop-cock, the contact between the sulphide and acid is restored, producing more of the gas.

Preparation of pure H_2S : (a) It is prepared by heating pure conc. HCl with antimony sulphide in a flask.

$$Sb_2S_3 + 6HCl \rightarrow 2SbCl_3 + 3H_2S$$

(b) It can also be obtained by the action of dil. HCl on sodium sulphide.

$$Na_2S + 2HCl = 2NaCl + H_2S$$

Collection : It is collected by displacement of water.

Properties : (i) It is a colourless gas, having a smell which resembles with that of rotten's eggs.

(ii) It is heavier than air (V.D. of air = 14·4) having vapour density 17.

(iii) It is fairly soluble in water.

(iv) It liquefies to colourless liquid at 12°C and 15 atmospheric pressure.

(v) It is highly poisonous gas.

CHEMICAL PROPERTIES OF H_2S

[A] As an acid

[B] as a dibasic acid

[C] as a reducing agent

[D] as an analytical reagent

(A) *As an acid* : (a) It acts as an acid because it turns moist blue litmus red.

(b) It dissociates incompletely. Hence it is a weak acid. Its dissociation constant is very low.

$$H_2S \rightleftharpoons 2H^+ + S^{-2}$$

(B) *As dibasic acid* : It acts as a dibasic acid because

(i) it dissociates in two stages as

$$H_2S \rightleftharpoons H^+ + HS^{-1} \quad K_A{}^I = \frac{[H^+]\,[HS^{-1}]}{[H_2S]} = \sim 10^{-7}$$

$$HS^{-1} \rightleftharpoons H^+ + S^{-2} \quad K_A^{II} = \frac{[H^+]\,[S^{-2}]}{[HS^-]} = \sim 10^{-14}$$

(ii) It forms one acid salt ($NaHS$) and one normal salt (Na_2S) with $NaOH$, hence it is a dibasic acid

$$\underset{\text{Sod. bisulphide}}{NaOH + H_2S \longrightarrow NaHS} \quad + H_2O$$

$$\underset{\text{Sod. sulphide}}{2NaOH + H_2S \longrightarrow Na_2S} \quad + 2H_2O$$

Similar reaction takes place with potassium hydroxide (caustic potash—KOH).

(c) *As a reducing agent* : H_2S is a reducing agent because (i) it is oxidised to sulphur with oxidising agents and (ii) it loses electrons during a chemical reaction.

$$\begin{array}{l} H_2S \longrightarrow 2H^+ + S^{-2} \\ S^{-2} \longrightarrow S^0 + 2e \\ \hline H_2S \longrightarrow 2H^+ + S + 2e \end{array}$$

(i) *Reaction with* X_2 ($X = Cl$, Br, I) :

$$H_2S + X_2 \rightarrow 2HX + S$$
$$(S^{-2} + X_2 \rightarrow 2X^{-1} + S)$$

(ii) *Reaction with Ferric salts* : It reduces ferric salts to ferrous salts.

$$2FeCl_3 + H_2S \rightarrow S + 2FeCl_2 + 2HCl$$
$$(2Fe^{+3} + S^{-2} \rightarrow S + 2Fe^{+2})$$
$$Fe_2(SO_4)_3 + H_2S \rightarrow 2FeSO_4 + H_2SO_4 + S$$

(iii) *Reaction with* HNO_3, H_2SO_4, PbO_2 etc. :

$$2HNO_3 + H_2S \rightarrow S + 2NO_2 + 2H_2O$$
$$(2NO_3^{-1} + S^{-2} + 4H^+ \rightarrow S + 2NO_2 + 2H_2O)$$
$$H_2SO_4 + H_2S \rightarrow S + SO_2 + 2H_2O$$
$$(SO_4^{-2} + S^{-2} + 4H^+ \rightarrow S + SO_2 + 2H_2O)$$
$$PbO_2 + H_2S \rightarrow PbO + H_2O + S$$
$$(PbO_2 + S^{-2} + 2H^+ \rightarrow PbO + H_2O + S)$$

(iv) *Reaction with* $KMnO_4$: When H_2S is passed into the acidified solution of potassium permanganate, then the later is decolourised and sulphur is obtained.

$$\begin{array}{c} 2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5\text{‘}O\text{’} \\ 5H_2S + 5\text{‘}O\text{’} \rightarrow 5H_2O + 5S \\ \hline 2KMnO_4 + 5H_2S + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5S \end{array}$$
$$(2MnO_4^{-1} + 16H^+ + 5S^{-2} \rightarrow 5S + 2Mn^{+2} + 8H_2O + 5S)$$

(v) *Reaction with* $K_2Cr_2O_7$ *solution* : When H_2S is passed into the orange acidified solution of $K_2Cr_2O_7$ then green colour solution of $Cr_2(SO_4)_3$ is obtained.

$$\begin{array}{c} K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3\text{‘}O\text{’} \\ 3H_2S + 3\text{‘}O\text{’} \rightarrow 3H_2O + 3S \\ \hline K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \rightarrow 3S + 7H_2O + K_2SO_4 + Cr_2(SO_4)_3 \end{array}$$
$$(Cr_2O_7^{-2} + 14H^+ + 3S^{-2} \rightarrow 3S + 2Cr^{+3} + 7H_2O)$$

(vi) *Reaction with SO_2* : It reacts with H_2S to give sulphur.

$$2H_2S+SO_2\rightarrow 3S+2H_2O$$
$$(2S^{-2}+SO_2+4H^+\rightarrow 3S+2H_2O)$$

(D) *As an analytical reagent* : (a) It gives precipitate with the following salts in dil. HCl medium.

$$M(NO_3)_2+H_2S\rightarrow MS\downarrow+2HNO_3\ (M=Hg^{+2}, Pb^{+2}, Cu^{+2})$$
$$CdCl_2+H_2S\rightarrow CdS\text{(Black) (yellow)}+2HCl$$
$$2BiCl_3+3H_2S\rightarrow Bi_2S_3\text{ (brown)}+6HCl$$
$$2SbCl_3+3H_2S\rightarrow Sb_2S_3\text{ (orange)}+6HCl$$

(b) It gives precipitate with the following salts in alkaline medium (NH_4Cl and NH_4OH).

$$MSO_4+H_2S\rightarrow MS\text{ (black)}+H_2SO_4(M=Ni^{+2}, CO^{+2})$$
$$ZnSO_4+H_2S\rightarrow ZnS\text{ (white)}+H_2SO_4$$
$$MnCl_2+H_2S\rightarrow MnS\text{ (pink)}+2HCl$$

Other chemical properties :

(i) It dissociates on heating.

$$H_2S\rightarrow H_2+S$$

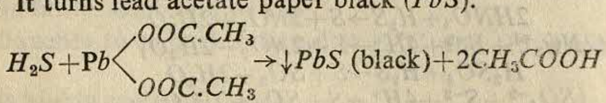
(ii) It does not support combustion but itself burns with a blue flame in the presence of oxygen.

$$2H_2S+3O_2\rightarrow 2H_2O+2SO_2\text{ (excess of }O_2)$$
$$2H_2S+O_2\rightarrow H_2O+2S\text{ (little of }SO_2)$$

(iii) It reacts with metals forming sulphides.

$$2Ag+H_2S\rightarrow Ag_2S+H_2$$
$$Sn+H_2S\rightarrow SnS+H_2$$

Test : It turns lead acetate paper black (PbS).



$$H_2S+\text{Pb}\begin{cases}OOC.CH_3\\OOC.CH_3\end{cases}\rightarrow\downarrow PbS\text{ (black)}+2CH_3COOH$$

Desiccation : It is desiccated by anhydrous P_2O_5.

Uses : (i) As a reducing agent. (ii) As a reagent in qualitative analysis.

Composition : It contains its own volume of hydrogen at S.T.P.

$$\underset{22400\text{ cc}}{H_2S}\rightarrow\underset{22400\text{ cc}}{H_2}+S$$

9.6. Typical Problems

Explain the following :

1. H_2S is not prepared in the laboratory by the action of HNO_3 on iron sulphide (FeS).

2. H_2S is not prepared in the laboratory by the action of conc. H_2SO_4 on FeS.

3. H_2O is a liquid but H_2S is a gas.

Solution : (1) Since H_2S is a reducing agent and HNO_3 is an oxidising agent, hence both reacts to give sulphur i.e. H_2S is oxidised by HNO_3.

$$FeS + HNO_3 \rightarrow Fe(NO_3)_3 + H_2S$$
$$\underset{\text{R.A.}}{H_2S} + \underset{\text{O.A.}}{HNO_3} \rightarrow S + NO_2 + H_2O$$

(2) Since H_2S is a reducing agent and conc. H_2SO_4 is an oxidising agent, hence both reacts to give sulphur.

$$H_2S + H_2SO_4 \rightarrow 2H_2O + S + SO_2$$

(3) See hydrogen bond (chapter 4).

4. Give reasonings—Why H_2S is not desiccated by (a) quick lime, (b) conc. H_2SO_4 and (c) $ZnCl_2$?

Solution : H_2S is an acidic gas and quick lime is a basic oxide, hence both reacts together.

$$CaO + H_2S \rightarrow CaS + H_2O$$

(b) H_2S is a reducing agent and conc. H_2SO_4 is an oxidising agent, hence both reacts to give sulphur.

$$H_2S + H_2SO_4 \rightarrow 2H_2O + S + SO_2$$

(c) H_2S reacts with $ZnCl_2$ to give white precipitate of ZnS, hence it cannot be used for desiccation of H_2S.

$$ZnCl_2 + H_2S \rightarrow \downarrow ZnS \text{ (white)} + 2HCl$$

9.7. Sulphur Dioxide

Mol. Formula : SO_2 Mol. wt. : 64

Preparation :

1. **Laboratory Method :** It is prepared by the action of conc. H_2SO_4 with copper turnings or foils in a flask containing a thistle funnel and a tube bent twice at right angles as shown in fig. 9.6.

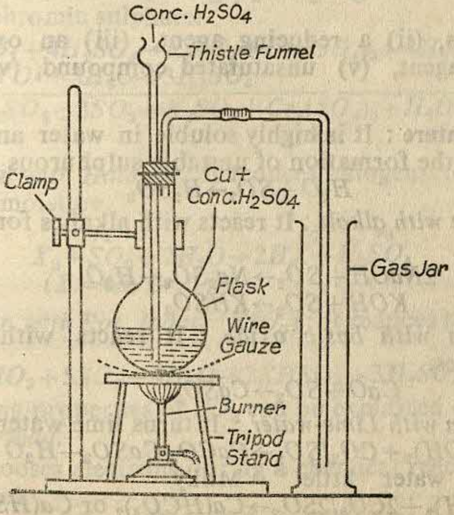


Fig. 9.6.

Copper turnings are placed in the flask and conc. H_2SO_4 is added in the flask through thistle funnel. On heating the flask SO_2 is evolved which is dried by passing through conc. H_2SO_4.

$$Cu+2H_2SO_4\xrightarrow{\text{heat}}CuSO_4+SO_2\uparrow+2H_2O$$

The gas is collected by upward displacement of air because it is heavier than air.

Other Methods : SO_2 can be prepared by :

(i) the action of dil. HCl on metal sulphites or bisulphites :

$$Na_2SO_3+2HCl\rightarrow 2NaCl+H_2O+SO_2$$

(ii) The action of conc. and hot H_2SO_4 on carbon, mercury, copper, silver etc.

$$C+2H_2SO_4\rightarrow CO_2+2SO_2+2H_2O$$
$$Hg+2H_2SO_4\rightarrow HgSO_4+SO_2+2H_2O$$
$$2Ag+2H_2SO_4\rightarrow Ag_2SO_4+SO_2+2H_2O$$

(iii) Roasting of iron pyrite (FeS_2) :

$$FeS_2+5\text{'}O\text{'}\rightarrow FeO+2SO_2\ [\times 2]$$
$$2FeO+\text{'}O\text{'}\rightarrow Fe_2O_3$$
$$\overline{2FeS_2+11\text{'}O\text{'}\rightarrow 4SO_2+Fe_2O_3}$$

or $$4FeS_2+11O_2\rightarrow 8SO_2+2Fe_2O_3$$

Properties : (A) **Physical** : (i) It is a colourless gas with suffocating smell of burning sulphur and is poisonous.

(ii) It is readily soluble in water.

(iii) It may be easily liquefied to a colourless liquid which boils at $-10°C$ and freezes at 75°C.

(B) **Chemical** : The chemical properties of SO_2 can be discussed as :

(i) acidic gas, (ii) a reducing agent, (iii) an oxidising agent, (iv) bleaching agent, (v) unsaturated compound, (vi) more acidic than CO_2.

(A) **Acidic nature** : It is highly soluble in water and its solution is acidic due to the formation of unstable sulphurous acid.

$$H_2O+SO_2\rightarrow H_2SO_3$$

(i) *Reaction with alkali* : It reacts with alkalies forming sulphites and bisulphites.

$$2NaOH+SO_2\rightarrow Na_2SO_3+H_2O$$
$$KOH+SO_2\rightarrow KHSO_3$$

(ii) *Reaction with basic oxide* : It reacts with basic oxides forming sulphites.

$$CaO+SO_2\rightarrow CaSO_3$$

(iii) *Reaction with Lime-water* : It turns lime water milky.

$$\underset{\text{Lime water}}{Ca(OH)_2}+\underset{\text{little}}{CO_2/SO_2}\rightarrow \underset{\text{Milky}}{CaCO_3/CaSO_3}+H_2O$$

$$Ca(OH)_2+2CO_2/2SO_2\rightarrow Ca(HCO_3)_2 \text{ or } Ca(HSO_3)_2$$

(B) As reducing agent : In presence of moisture, it acts as a strong reducing agent. This is due to *liberation of nascent hydrogen.*

$$SO_2+2H_2O \rightarrow H_2SO_4+2\text{'}H\text{'}$$

Similarly, it absorbs oxygen in presence of an oxidising agent :

$$SO_2+H_2O+\text{'}O\text{'} \rightarrow H_2SO_4$$

Hence under both the conditions, it acts as a powerful reducing agent.

(i) *Reaction with Ferric salts* : (a) SO_2 reduces ferric chloride solution to ferrous chloride :

$$\begin{array}{c} SO_2+2H_2O \rightarrow H_2SO_4+2\text{'}H\text{'} \\ 2FeCl_3+2\text{'}H\text{'} \rightarrow 2FeCl_2+2HCl \\ \hline 2FeCl_3+2H_2O+SO_2 \rightarrow 2FeCl_2+H_2SO_4+2HCl \end{array}$$

(b) Ferric sulphate is reduced to Ferrous sulphate by SO_2 in presence of water.

$$\begin{array}{c} SO_2+2H_2O \rightarrow H_2SO_4+2\text{'}H\text{'} \\ Fe_2(SO_4)_3+2\text{'}H\text{'} \rightarrow 2FeSO_4+H_2SO_4 \\ \hline Fe_2(SO_4)_3+SO_2+2H_2O \rightarrow 2FeSO_4+2H_2SO_4 \end{array}$$

(ii) *Reaction with Pot. Permanganate* : It decolouries acidified potassium permanganate solution in cold.

$$\begin{array}{l} 2KMnO_4+3H_2SO_4 \rightarrow K_2SO_4+2MnSO_4+3H_2O+5'O' \\ 5SO_2+5'O'+5H_2O \rightarrow 5H_2SO_4 \\ \hline \underbrace{2KMnO_4}_{\text{violet}}+5SO_2+2H_2O \rightarrow 2H_2SO_4+K_2SO_4+\underbrace{2MnSO_4}_{\text{colourless}} \end{array}$$

(iii) *Reaction with Pot. Dichromate* : It reduces acidified solution of potassium dichromate (orange) giving a green solution due to the formation of chromic sulphate.

$$\begin{array}{l} K_2Cr_2O_7+4H_2SO_4 \rightarrow K_2SO_4+Cr_2(SO_4)_3+4H_2O+3'O' \\ 3SO_2+3'O'+3H_2O \rightarrow 3H_2SO_4 \\ \hline K_2Cr_2O_7+H_2SO_4+3SO_2 \rightarrow K_2SO_4+Cr_2(SO_4)_3+H_2O \end{array}$$

orange green

(iv) *Reaction with Halogen* : It reduces halogens to halogen acid in presence of moisture.

$$\overset{0}{X_2}+\overset{+4}{S}O_2+2H_2O \rightarrow 2H\overset{-1}{X}+H_2\overset{+6}{S}O_4$$
$$(X=Cl,\ Br,\ I)$$

(v) *Reaction with Pot. Iodate* (KIO_3) : It reduces potassium iodate to iodine.

$$2KIO_3+5SO_2+4H_2O \rightarrow 2KHSO_4+3H_2SO_4+I_2$$

The reducing properties of SO_2 can be explained on the basis of *ion-electron method.*

Since SO_2 looses electrons during a chemical reaction, hence it is a reducing agent.

$$SO_2+2H_2O \rightarrow SO_4^{-2}+4H^{+}+2e$$

(i) *Reaction with Cl_2* :

$$\begin{array}{r} Cl_2+2e\rightarrow 2Cl^{-1} \\ SO_2+2H_2O\rightarrow SO_4^{-2}+4H^++2e \\ \hline SO_2+2H_2O+Cl_2\rightarrow SO_4^{-2}+4H^++2Cl^{-1} \end{array}$$

(ii) *Reaction with $KMnO_4$* :

$$\begin{array}{r} MnO_4^{-1}+8H^++5e\rightarrow Mn^{+2}+4H_2O\ [\times 2] \\ SO_2+2H_2O\rightarrow SO_4^{-2}+4H^++2e\ [\times 5] \\ \hline 2MnO_4^{-1}+5SO_2+2H_2O\rightarrow 5SO_4^{-2}+4H^++2Mn^{+2} \end{array}$$

(C) *As an oxidising agent* : It acts as an oxidising agent because it gives sulphur with reducing agent.

(i) *Reaction with Mg* : When a piece of burning magnesium wire is taken in a jar of sulphur dioxide it forms magnesium oxide and fine particles of sulphur are deposited on the walls of the jar.

$$2Mg+SO_2\rightarrow 2MgO+S$$

(ii) *Reaction with H_2S* : It reacts with H_2S to give sulphur.

$$2H_2S+SO_2\rightarrow 3S+2H_2O$$

(iii) *Reaction with HI* : It reacts with *HI* to give Iodine.

$$4HI+SO_2\rightarrow 2H_2O+S+2I_2$$

The oxidising properties of SO_2 can be explained on the basis of ion-electron method.

Since SO_2 gains electrons during a chemical reaction, hence it acts as an oxidising agent.

(i) *Reaction with H_2S* :

$$\begin{array}{r} SO_2+4H^++4e\rightarrow S+2H_2O \\ S^{-2}\rightarrow S+2e\ [\times 2] \\ \hline SO_2+4H^++2S^{-2}\rightarrow 3S+2H_2O \end{array}$$

(ii) *Reaction with Mg* :

$$\begin{array}{r} SO_2+4H^++4e\rightarrow S+2H_2O \\ Mg\rightarrow Mg^{+2}+2e\ [\times 2] \\ \hline 2Mg+SO_2+4H^+\rightarrow 2Mg^{+2}+S+2H_2O \end{array}$$

(D) As an antichlor : It is known as antichlor since it destroys the properties of chlorine.

$$SO_2+Cl_2+2H_2O\rightarrow H_2SO_4+2HCl$$

(E) As an unsaturated compound (Addition Reaction) : Sulphur is hexavalent but only four valencies of sulphur are satisfied in SO_2 and the remaining two valencies of sulphur remain unsatisfied. This makes SO_2 an unsaturated compound.

(i) It reacts with chlorine in presence of sun light forming sulphuryl chloride.

$$SO_2+Cl_2\rightarrow SO_2Cl_2$$

(ii) It forms an addition product with sodium peroxide.

$$Na_2O_2+SO_2\rightarrow Na_2SO_4$$

(iii) In presence of platinum, Vanadium pentoxide or $MnSO_4$ as catalyst, it combines with atmospheric oxygen to form sulphur trioxide.

$$2SO_2+O_2 \rightarrow 2SO_3$$

(F) **As Bleaching Agent** : In the presence of moisture it possesses strong bleaching properties. It decolourises vegetable colouring matter to colourless reduction products. On standing in air, the colourless reduced product is re-oxidised by atmospheric oxygen to regain its original colour. It bleaches due to *reduction* and the bleaching is *temporary*.

$$SO_2+2H_2O \rightarrow H_2SO_4+2'H'$$

Coloured substance + $'H' \rightarrow$ Colourless (reduction product)
↓ air
Coloured

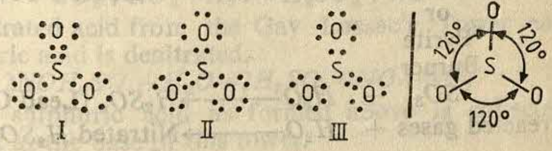
Tests : (i) It can be detected by its characteristic suffocating smell of burning sulphur.

(ii) It turns acidified potassium dichromate paper green and lime water milky.

(iii) It decolourises acidified solution of Potassium permaganate.

Uses : (i) In the manufacture of H_2SO_4 by contact process.
(ii) As a bleaching agent.
(iii) As a disinfectant and household fumigation.
(iv) As a refrigerant.
(v) In the refining of sugar.

Structure : The molecule of sulphur dioxide is asymmetrical with an $O-S-O$ bond angle of 120°. It may be considered as resonance hybrid of the following three forms.



Sulphur dioxide contains its volume own volume of oxygen at S.T.P.

$$\underset{20\ cc}{SO_2} \rightarrow S + \underset{20\ cc}{O_2}$$

9.8. SULPHURIC ACID, H_2SO_4

Mol. Formule—H_2SO_4 Mol. Wt.—98

History : It was known as early as in 8th century and was prepared from green vitriol ($FeSO_4.7H_2O$). In 1842 Gay Lussac Tower and in 1850 Glover Tower were used in the manufacture of this acid.

Methods for the Preparation of H_2SO_4 :

(i) *By the action of water on sulphur trioxide* :

It is formed by dissolving sulphur trioxide in water.

$$SO_3+H_2O \rightarrow H_2SO_4$$

(ii) *By the action H_2O_2 on SO_2* : It is formed by the action of sulphur dioxide on H_2O_2.

$$SO_2+H_2O_2 \rightarrow H_2SO_4$$

(iii) *By the oxidation of sulphur dioxide* : It is also formed by the oxidation of sulphur dioxide.

$$2SO_2+2H_2O+O_2 \rightarrow 2H_2SO_4$$
$$SO_2+2H_2O+Cl_2 \rightarrow H_2SO_4+2HCl$$
$$SO_2+2HNO_2 \rightarrow H_2SO_4+2NO$$

Laboratory Preparation of H_2SO_4 : The principle of the preparation of H_2SO_4 in the laboratory is the same as Lead Chamber Process.

Manufacture of sulphuric acid : It is manufactured by :

(A) *Lead chamber Process*, (B) *Contact Process*.

(A) **Lead Chamber Process** :

Principle : In this process sulphur dioxide is obtained by burning sulphur or roasting iron pyrites. It is oxidised to sulphur trioxide by the oxides of nitrogen. Sulphur trioxide so obtained reacts with water to form sulphuric acid. The reaction theory gives the following explaination.

(a) (i) $$\underset{\text{Sulphur or Pyrite Burner}}{SO_2} + \underset{\text{Nitre Pot}}{NO_2} \longrightarrow \underbrace{SO_3 + NO}_{\text{Glover's Tower}}$$

(ii) $$SO_3 + H_2O \longrightarrow H_2SO_4 \text{ (Lead Chamber)}$$

(iii) $$\text{Unreacted gases} + H_2O \longrightarrow \text{Nitrated } H_2SO_4 \text{ (Gay Lussac's Tower)}$$

This nitrated sulphuric acid is sent to Glover's Tower and the process is repeated.

or (b) Nitric oxide reacts with oxygen to form Nitrogen peroxide (NO_2). This reacts with SO_2 and water vapour to form sulphonitronic acid (H_2SO_5).

$$2NO+O_2 \rightleftharpoons 2NO_2;\ SO_2+H_2O \rightleftharpoons H_2SO_3$$
$$H_2SO_3+NO_2 \rightarrow H_2SNO_5$$

This reacts with NO_2 and O_2 to give nitrosil hydrogen sulphate or nitrososulphuric acid or chamber crystal ($NOHSO_4$).

$$2H_2SNO_5+NO_2 \rightarrow 2NOHSO_4+NO+H_2O$$
$$4H_2SNO_5+O_2 \rightarrow 4NOHSO_4+2H_2O$$

Some of the sulphonitric acid dissociates to give H_2SO_4.

$$H_2SNO_5 \rightleftharpoons H_2SO_4 + NO$$

The chamber crystal reacts with water vapour to give H_2SO_4.

$$4NOHSO_4 + 2H_2O \rightleftharpoons 4H_2SO_4 + 4NO + O_2$$

Description of the process :

(i) *Pyrites or Sulphur Burner* : These are brick furnaces in which sulphur or iron phyrites are burnt to produce sulphur dioxide.

$$S + O_2 \rightarrow SO_2$$
$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

(ii) *Dust chamber* : The dust particles are moistened with steam and become heavy and settle down. The gas thus breed from dust particles is passed through nitre pots.

(iii) *Nitre Pots* : Its function is to prepare NO_2.

These pots contain $NaNO_3$ and conc. H_2SO_4. The hot gases of pyrite burners are passed over the pots and carry along with them oxides of nitrogen which are produced by the reduction of nitric acid.

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$
$$2HNO_3 + SO_2 \rightarrow H_2SO_4 + 2NO_2$$

(iii) *Glover's Tower* : This is packed with flint stones. The hot gases from pyrite burner and nitre pots are passed through Glover's Tower. The nitrated H_2SO_4 from Gay Lussac's Tower is poured from the top of the Glover's Tower. The function of the tower is

(a) the incoming gases (NO_2, SO_2 etc.) are cooled to 70°C.

(b) SO_2 is oxidised to SO_3.

(c) dil. H_2SO_4 (coming from lead chambers) is concentrated.

$$SO_2 + NO_2 + H_2O \rightarrow H_2SO_4 + NO$$

(d) the nitrated acid from the Gay Lussac's Tower containing nitrososulphuric acid is denitrated.

$$2NOH_2SO_4 + H_2O \rightarrow 2H_2SO_4 + NO + NO_2$$

Concentrated sulphuric acid as formed above is collected in the reservoir built at the base of this tower.

(v) *Lead Chambers* : The gases from the Glover's Tower are passed into a set of lead chambers connected in series. These are made of lead sheets supported in wooden frame works and are rectangular in shape. The capacity of chamber is about 1,00,000 to 15,00,000 cubic feet.

Here the gases meet with steam or spray of water with the result that dilute H_2SO_4 is formed. Nitric oxide is formed by the interaction of SO_2, oxides of nitrogen and water which is oxidised to nitrogen peroxide by the atmospheric oxygen.

$$NO_2 + SO_2 \rightarrow SO_3 + NO$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$
$$2NO + O_2 \rightarrow 2NO_2$$

If water is not present in sufficient quantity, colourless crystals of nitrosulphuric acid are deposited on the walls of the chamber which react with steam and form sulphuric acid and oxides of nitrogen. These crystals are known as chamber crystals.

$$2SO_2+H_2O+3NO_2 \rightarrow 2NO.HSO_4+NO$$
$$2NOHSO_4+H_2O \rightarrow 2H_2SO_4+N_2O_3$$

(vi) *Gay Lussac's Tower* : It is packed with coke and from the top which trickles down concentrated sulphuric acid. The gaseous mixture from lead chamber containing oxides of nitrogen SO_2, SO_3 etc. react with H_2SO_4 to form nitrated sulphuric acid. The nitrated acid so obtained is pumped up to the top of the Glover's Tower for the recovery of oxides of nitrogen.

$$NO+NO_2+2H_2SO_4 \rightarrow 2NO.HSO_4+H_2O$$

The water gases from the Gay Lussac's Tower are passed out through a chimney fitted in the tower which acts as an aspirates and maintains a balance in the flow of gases throughout the plant.

Self Explainatory Diagram :

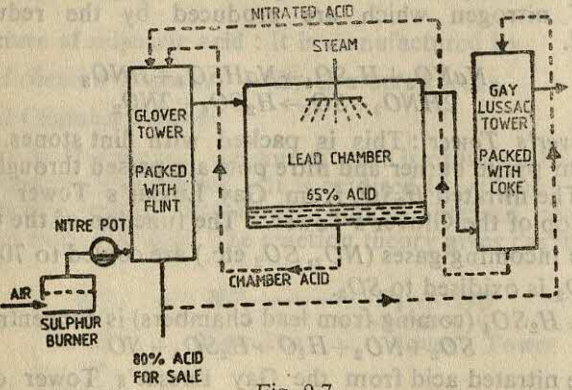


Fig. 9.7.

(B) The Contact Process :

Theory : If a mixture of pure and dry sulphur dioxide and oxygen (1 : 7) is passed over platinised asbestos or finely divided Pt or vanadium pentoxide V_2O_5 the gases camber to form sulphur trioxide.

$$2SO_2+O_2 \rightleftharpoons 2SO_3+45{,}200 \text{ cal.}$$

This reaction is reversible and exothermic and hence according to Le-chatelier principle the favourable conditions for the formation of sulphur trioxide (SO_3) is

(a) an excess of air, (b) a high pressure and (c) a low temperature.

The optimum temperature and pressure condition is 450°C – 500°C and 1·5 – 1·7 atmosphere pressure.

SO_3 is dissolved in conc. H_2SO_4 to obtain oleum or fuming H_2SO_4. This gives on dilution with water sulphuric acid of desired concentration.

$$SO_3+H_2SO_4 \rightarrow H_2S_2O_7$$
$$H_2S_2O_7+H_2O \rightarrow 2H_2SO_4$$

Working : The manufacture is carried out in three main stages.

(i) Preparation of pure SO_2, (ii) Conversion of SO_2 into SO_3, (iii) Conversion of SO_3 into $H_2S_2O_7$.

(i) *Preparation of pure* SO_2 :

(a) *Sulphur or Pyrite Burners* : In these burners sulphur dioxide is produced by burning sulphur or by roasting iron pyrites in a current of air :

$$S+O_2 \rightarrow SO_2$$
$$4FeS_2+11O_2 \rightarrow 2Fe_2O_3+8SO_2$$

(b) *Dust Chamber* : The gaseous mixture containing mainly sulphur dioxide and air is mixed with various impurities such as dust particles, finely divided sulphur, arsenic, water vapours and sulphuric acid. These impurities if present, are removed. These will poison the catalyst. In this chamber steam is blown in to make the dust particles settle down. Now the gaseous mixture free from dust particles inters the cooling pipes.

(c) *Cooling Pipes* : The gaseous mixture passes through a series of lead pipes when the temperature falls down to 100°C. This also helps in the precipitation of dust particles.

(d) *Scrubber or Washers* : Now the gases are led to scrubber which is filled with quartz pieces. The scrubber is provided with a tank containing cold water. The gases are washed by a down coming spray of water. The soluble impurities and H_2SO_4 fog are washed down along with dust particles, and the pure gaseous mixture are led to drying tower.

(e) *Drying Tower* : It is filled with quartz pieces or coke. The gases are dried by down-coming spray of conc. H_2SO_4. The gases are now passed to arsenic purifier.

(f) *Arsenic Purifier* : This tower contains precipitated ferric hydroxide placed on a number of horizontal shelves which remove any arsenic oxide present in the gases passing through it.

(g) *Tyndal Box or Testing Box* : This is a reactangular box blackened from inside. The dry and pure mixture of SO_2 and O_2 is then sent to the testing box in order to test the purity of the gas mixture. Here a strong beam of light is projected and if any particle in sulphur suspension are presnt they become visible due to Tyndal effect.

The pure and dry mixture of sulphur dioxide and oxygen free from all sorts of impurities is allowed to enter the contact chamber.

(ii) *Conversion of SO_2 into SO_3 : Contact Chamber :*

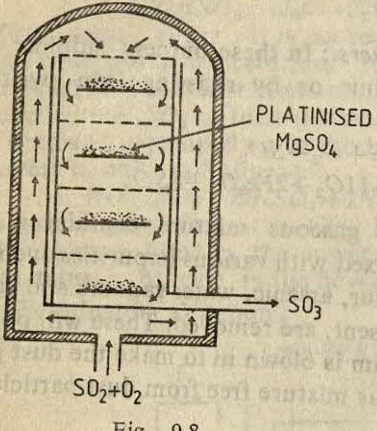


Fig. 9.8.

It is a big chamber made of iron containing a number of tubes each packed with platinised asbestos or vanadium pentoxide. The pure and dry mixture of sulphur dioxide and oxygen passes in the platinised asbestos tubes where the exchange of heat between the two takes place. In the presence of catalyst SO_2 is oxidised to SO_3 which leaves the contact chamber.

$$2SO_2+O_2\rightarrow 2SO_3+45{,}200 \text{ cal.}$$

(iii) *Conversion of SO_3 to $H_2S_2O_7$: Absorption Tower :*

SO_3 entering from the contact chamber meets in this tower a discending stream of 97% of sulphuric acid. It absorbs SO_3 forming oleum or fuming sulphuric acid. It can be diluted with water to obtain any required concentration of sulphuric acid.

$$SO_3+H_2O\rightarrow H_2SO_4$$
$$H_2SO_4+SO_3\rightarrow H_2S_2O_7$$
$$H_2S_2O_7+H_2O\rightarrow 2H_2SO_4$$

Self Explantory Diagram :

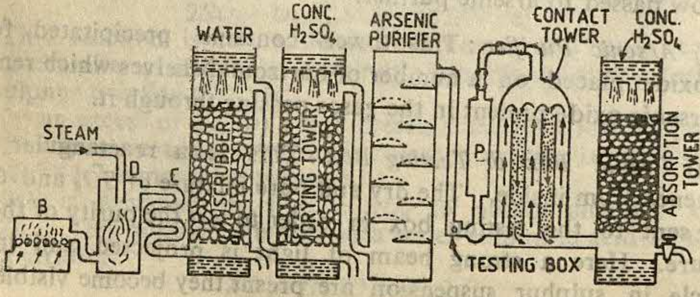


Fig. 9.9.

COMPARISION BETWEEN THE TWO PROCESSES USED FOR THE MANUFACTURE OF SULPHURIC ACID

Serial no.	*Lead chamber process*	*Contact Process*
1.	This method is cheape and easy.	This process is costly and tedious.
2.	The concentration of the acid is nearly 65·70°/₀.	The concentration of the acid is nearly 95°/₀.
3.	The acid contains many impurities and their removal is a difficult task.	The acid is pure.
4.	The acid needs concentration which is done by cascade and or Gaillard's process.	The acid does not require any concentration.

CONCENTRATION OF CHAMBER ACID : (Acid obtained)

From Lead chamber. It is concentrated by (a) cascade process, (b) Gaillard process.

(i) *Cascade Process* : In this process, the chamber acid is allowed over acid proof bricks. The dishes are so arranged that the acid passed from upper to the lower dish as it goes on concenrated.

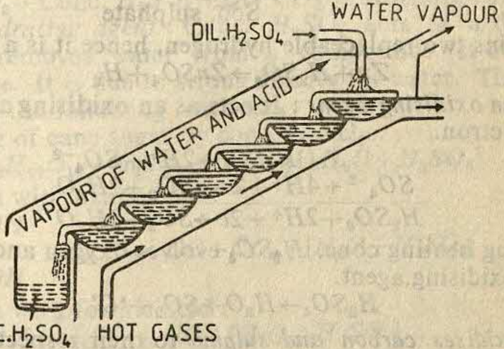


Fig. 9.10.

The acid gets concentrated by the hot gases rising up. As the acid goes down from dish to dish, it gradually gets concentrated till it is collected in a container placed below the last dish.

(ii) *Gaillard Process* : The acid is introduced in the form of spray from top of tower which is built of acid resisting stone. Hot air is passed from the lower side of the tower. During the passage downwards the droplets of the dilute acid lose their water molecules. By the time acid reaches the bottom of tower and it becomes 95% pure acid. The last drops of water are removed by adding SO_3 to the acid, which combines with water forming H_2SO_4.

Properties : *Physical* :

(i) It is a colourless, odourless, syrupy liquid. (ii) Therefore the acid boils at 339°C and freezes to 10·5°C. (iii) Its specific gravity is 1·84. (iv) The concentrated acid fumes in moist air. (v) It is a good conductor of electricity.

Chemical : The chemical property of sulphuric acid may be discussed under the following headings.

(1) As an acid, (2) As a dibasic acid, (3) As an oxidising agent (4) As a desiccating agent, (5) As a dehydrating agent, (6) As a sulphonating agent, (7) As a less volatile than HNO_3 or HCl, (8) Action of heat.

(1) *As an acid* : It turns blue litmus red. On adding water it dissociates as follows :

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^{-1};\ HSO_4^{-1} \rightleftharpoons H^+ + SO_4^{-2}$$

(2) *As dibasic acid* : It is a strong dibasic acid and forms two series of salts i.e. normal salt (Na_2SO_4) and acid salt ($NaHSO_4$) with $NaOH$.

$$NaOH + H_2SO_4 \rightarrow \underset{\text{Sod. hydrogen sulphate}}{NaHSO_4} + H_2O$$

$$2NaOH + H_2SO_4 \rightarrow \underset{\text{Sod. sulphate}}{Na_2SO_4} + 2H_2O$$

It contains two replaceable hydrogen, hence it is a dibasic acid.

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

(3) *As an oxidising agent* : It acts as an oxidising agent because it takes up electron.

$$\begin{array}{c} H_2SO_4 \rightarrow 2H^+ + SO_4^{-2} \\ SO_4^{-2} + 4H^+ + 2e \rightarrow SO_2 + 2H_2O \\ \hline H_2SO_4 + 2H^+ + 2e \rightarrow SO_2 + 2H_2O \end{array}$$

On strong heating conc. H_2SO_4 evolves oxygen and therefore, it acts as an oxidising agent.

$$H_2SO_4 \rightarrow H_2O + SO_2 + \text{'}O\text{'}$$

(i) It *oxidises carbon and sulphur* to their respective oxides and phosphorus into orthophospheric acid.

$$C + H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$$
$$(C + 2SO_4^{-2} + 4H^+ \rightarrow CO_2 + 2SO_2 + 2H_2O)$$
$$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$$
$$(S + 2SO_4^{-2} + 4H^+ \rightarrow 3SO_2 + 2H_2O)$$
$$2P + 5H_2SO_4 \rightarrow 2H_3PO_4 + 5SO_2 + 2H_2O$$
$$(2P + 5SO_4^{-2} + 10H^+ \rightarrow 2H_3PO_4 + 5SO_2 + 2H_2O)$$
$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$$
$$(Cu + 2SO_4^{-2} + 4H^+ \rightarrow Cu^{+2} + SO_2 + 2H_2O)$$

(ii) It *oxidises* a number of compounds. *Iodides* and *bromides* are *oxidised to iodine and bromine* respectively, halogen acids to halogen and hydrogen sulphide to sulphur.

(i) $2NaBr+2H_2SO_4\xrightarrow{\text{heat}}Na_2SO_4+SO_2+2H_2O+Br_2$

$(2Br^{-1}+SO_4^{-2}+4H^+\longrightarrow SO_2+Br_2+2H_2O)$

(ii) $2NaI+2H_2SO_4\xrightarrow{\text{heat}}Na_2SO_4+SO_2+2H_2O+I_2$

$(2I^{-1}+SO_4^{-2}+4H^+\longrightarrow SO_2+I_2+2H_2O)$

(iii) $H_2S+H_2SO_4\longrightarrow S+SO_2+2H_2O$

$(S^{-2}+SO_4^{-2}+4H^+\longrightarrow I_2+SO_2+2H_2O)$

Dil. H_2SO_4 is also an oxidising agent.

$$\begin{array}{l} H_2SO_4\rightarrow 2H^++SO_4^{-2} \\ \underline{2H^++2e\rightarrow H_2} \\ H_2SO_4+2e\rightarrow H_2+SO_4^{-2} \end{array}$$

It gives hydrogen with metals which are above hydrogen in the electrochemical series (common metals) which are below H_2 in E.C.S. (*Cu*, *Hg*, *Ag*, *Au*, *Pt*).

$$\overset{0}{Zn}+\overset{+2}{H_2}SO_4\rightarrow ZnSO_4+\overset{0}{H_2}$$

In this case zinc is oxidised to Zn^{++} and H^+ is reduced to H_2. Hence H_2SO_4 acts as an oxidising agent.

(4) *As a desiccating agent* : Conc. H_2SO_4 is used as a desiccating agent for acidic gases because it has strong affinity for water.

Moist Cl_2+Conc. $H_2SO_4\rightarrow$Dry Cl_2+[Moisture+H_2SO_4]

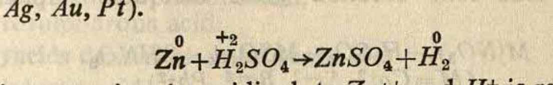
Moist CO_2+Conc. $H_2SO_4\rightarrow$Dry CO_2+[Moisture+H_2SO_4]

(5) *As dehydrating agent* : Conc. H_2SO_4 acts as a dehydrating agent and it removes water from a compound. It brings about chemical change. It is due to strong affinity for water. This property is illustrated by the following reactions.

(i) Charring of cane sugar by conc. H_2SO_4.

$$C_{12}H_{22}O_{11}+H_2SO_4\rightarrow 12C+[11H_2O+H_2SO_4]$$

(ii) Reaction with oxalic acid :



$$\begin{array}{c} COOH \\ | \\ COOH \end{array}+H_2SO_4\rightarrow CO+CO_2+[H_2O+H_2SO_4]$$

(iii) Reaction with formic acid :

$$HCOOH+H_2SO_4\rightarrow CO+[H_2O+H_2SO_4]$$

(iv) Reaction with ethyl alcohol :

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH}+H_2SO_4\xrightarrow{160°C}\underset{\text{Ethylene}}{C_2H_4}+[H_2O+H_2SO_4]$$

(6) *As sulphonating agent* : Conc. H_2SO_4 is used in the sulphonation of Benzene.

$$\underset{\text{Benzene}}{C_6H_6}+\underset{\text{Sulphuric acid}}{HOSO_3H}\rightarrow\underset{\text{Benzene sulphonic acid}}{C_6H_5SO_3H}+H_2O$$

(7) *As less volatile than HNO_3 and HCl :*

Conc. H_2SO_4 is less volatile than HNO_3 or HCl because H_2SO_4 has higher boiling point than HNO_3 or HCl. Therefore, it is used in the preparation of these acids from metal nitrates and chlorides.

$$2NaNO_3+H_2SO_4\xrightarrow{\text{heat}}Na_2SO_4+2HNO_3$$

$$2NaCl+H_2SO_4\xrightarrow{\text{heat}}Na_2SO_4+2HCl$$

(8) *Action of heat* : Conc. H_2SO_4 when heated gives SO_2 and O_2.

$$2H_2SO_4\rightarrow2H_2O+2SO_2+O_2$$

Fuming sulphuric acid : SO_3 is dissolved in conc. H_2SO_4 then pyro sulphuric acid is obtained.

$$H_2SO_4+SO_3\rightarrow H_2S_2O_7$$

This is known as fuming sulphuric acid.

Precipitation of insoluble salts of sulphate : Calcium, strontium, barium and lead salts solution gives insoluble sulphates with dil. H_2SO_4.

$$M(NO_3)_2+H_2SO_4\rightarrow MSO_4\downarrow+2HNO_3$$
$$(M=Ca^{+2}, Sr^{+2}, Ba^{+2}, Pb^{+2})$$

Test : (i) Conc. H_2SO_4 gives SO_2 when heated with copper. The gas turns moist dichromate paper green.

(ii) Sulphuric acid gives white precipitate with barium chloride solution which is insoluble in mineral acids.

(iii) H_2SO_4 gives white precipitate with lead nitrate solution.

Uses : (i) For the manufactured of calcium superphosphate and ammonium sulphate which are important fertilisers.

(ii) In the refining of petroleum.

(iii) In the manufacture of HNO_3, HCl etc.

(iv) In the manufacture of paints, drugs, dyes, disinfection, textiles and rayon.

(v) In the lead storage batteries.

(vi) As a dehydrating and desiccating agent.

TO PROVE THAT SULPHURIC ACID CONTAINS HYDROGEN, OXYGEN AND SULPHUR

Conc. sulphuric acid is allowed to drop on hot pumice stone, when the acid decomposes into gases. The gases are allowed to pass in succession through two U-tubes—one placed in water at ordinary room temperature and the other in a freezing mixture. Liquids will collect in the two U-tubes. The liquid in the first U-tube is shown to be water by its action on anhydrous copper sulphate (turns blue) and in the second U-tube is shown to be SO_2 by its smell and action on acidified potassium dichromate solution (turns from *orange to* *green).* The gas issuing out of the second U-tube is shown to be oxygen by its power of re-kindling a glowing piece of wood and its absorption by alkaline pyrogallate solution. Now that, water and sulphur dioxide have been formed from sulphuric acid alone, hydrogen and sulphur must be the constituents to the acid.

9.9. Oxyacids of Sulphur

Sulphur has a very large number of oxyacids indeed. There are more than one opinion on the structure of several of the sulphur oxyacids. Many of the acids exist in solution only although their salts are well characterised. A particularly interesting group of sulphur oxyacids have sulphur-sulphur linkage. These acids are known as thionic acids and have two to six sulphur atoms in the chain. Some representative sulphur oxyacids with their structures are given below :

1. Oxyacids derived from sulphurous acid :

(a) Sulphurous acid,
(b) Hypo/hydrosulphurous acid,
(c) Pyrosulphurous acid.

2. Oxyacids derived from sulphuric acid ;

(a) Sulphuric acid,
(b) Thiosulphuric acid,
(c) Pyrosulphuric acid.

3. Thionic oxyacids :

(a) Dithionic acid,
(b) Polythionic acid.

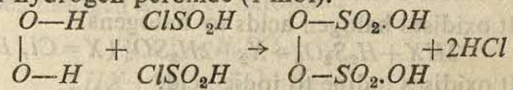
4. Peroxy acids :

(a) Peroxy monosulphuric acid,
(Caro's acid)
(b) Peroxydisulphuric acid,
(Marshall's acid)

Perdisulphuric acid or Peroxydisulphuric acid, or Marshall's acid.

Preparation :

(a) *From chlorosulphonic acid* : By the action of chlorosulphonic acid (2 mols) on hydrogen peroxide (1 mol).



$$\begin{array}{l} O-H \\ | \\ O-H \end{array} + \begin{array}{l} ClSO_2H \\ \\ ClSO_2H \end{array} \rightarrow \begin{array}{l} O-SO_2.OH \\ | \\ O-SO_2.OH \end{array} + 2HCl$$

(b) *By the electrolysis of sulphuric acid* : When 50-60% H_2SO_4 is submitted to electrolysis at a low temperature and high current density then HSO_4 ions unite at anode to give perdisulphuric acid.

$$H_2SO_4 \rightleftharpoons \underset{\text{Cathode}}{H^+} + \underset{\text{Anode}}{HSO_4^{-1}}$$

Cathode : $H^+ + e \rightarrow H; \quad H + H \rightarrow H_2$

Anode : $2HSO_4^{-1} \rightarrow 2HSO_4 + 2e \rightarrow H_2S_2O_8$

Apparatus : It consists of :

Electrolyte : 50-60% H_2SO_4 in a large size test tube.

Anode : Platinum wire surrounded by a glass tube open at both ends. The tube acts as diaphragm.

Cathode : A spiral of copper wire wound round the diaphragm.

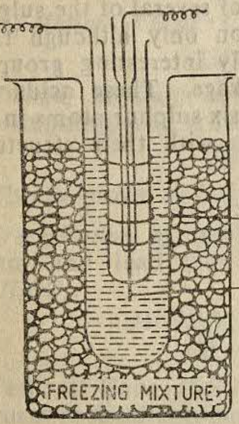


Fig. 9.9.

Description : 50-60% H_2SO_4 is taken in a large size test-tube and placed in a beaker containing ice. In this test-tube is placed a tube open at both ends. It acts as a diaphragm. A spiral of copper wire is wound round it. A platinum wire fused in a capillary is placed in it. On passing an electric current a solution containing perdisulphuric acid is obtained.

Properties : (i) *Physical* :

(a) *State* : It is colourless crystalline hygroscopic solid. Its melting point is 65°C.

(b) *Stability* : It is fairly stable but loses O_2 on warming.

$$2H_2S_2O_8 \rightarrow 2H_2SO_4 + 2SO_2 + O_2$$

(ii) *Chemical* :

(a) *Hydrolysis* : It is hydrolysed on keeping the solution. It forms Caro's acid on hydrolysis.

$$H_2S_2O_8 + H_2O \rightarrow H_2SO_4 + H_2SO_5$$

(b) *Distillation with dil.* H_2SO_4 : It gives H_2SO_4 and H_2O_2

$$H_2S_2O_8 + 2H_2O \rightarrow 2H_2SO_4 + H_2O_2$$

$$S_2O_8^{-2} + 2e^- \rightarrow 2SO_4^{-2}$$

(c) *An oxidising agent* : (i) It oxidises KI to I_2 very slowly.

$$2KI + H_2S_2O_8 \rightarrow K_2SO_4 + H_2SO_4 + I_2$$

(ii) It oxidises aniline to aniline black.

(iii) It oxidises halogen acids to halogens.

$$2HX + H_2S_2O_8 \rightarrow X_2 + 2H_2SO_4 \ (X = Cl, Br, I)$$

(iv) It oxidises iodine to iodic acid.

$$I_2 + 5H_2S_2O_8 + 6H_2O \rightarrow 2HIO_3 + 10H_2SO_4 + H_2$$

(v) It oxidises ferrous salts to ferric salts and chromic salts to chromate.

$$2FeSO_4 + H_2S_2O_8 \rightarrow Fe_2(SO_4)_3 + H_2SO_4$$

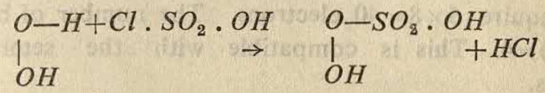
Its salts oxidise salts of silver, lead, manganese, cobalt and nickel into metallic peroxide.

$$K_2S_2O_8+2AgNO_3+H_2O \rightarrow Ag_2O_2+2KHSO_4+2HNO_3$$
$$K_2S_2O_8+MnCl_2+2H_2O \rightarrow MnO_2+2KHSO_4+2HCl$$

Structure : See table.

PER MONOSULPHURIC ACID OR PEROXYMONO SULPHURIC ACID OR CARO'S ACID

Preparation : 1. It may be obtained by the action of hydrogen peroxide (1 mol) on calculated quantity of chlorosulphonic acid (1 mol).



$$\begin{array}{l} O-H+Cl\,.\,SO_2\,.\,OH \\ | \\ OH \end{array} \rightarrow \begin{array}{l} O-SO_2\,.\,OH \\ | \\ OH \end{array} +HCl$$

2. It may also be obtained by allowing to stand a mixture of concentrated sulphuric acid and potassium perdisulphate for an hour and powering the mixture over ice.

$$K_2S_2O_8+H_2SO_4 \rightarrow H_2S_2O_8+K_2SO_4$$
$$H_2S_2O_8+H_2O \rightarrow H_2SO_5+H_2SO_4$$

Properties : 1. The anhydrous acid is a white crystalline solid. It melts at 45°C. It keeps well for few days and afterwards reduces to oxygen slowly.

2. It rapidly evolves oxygen with hydrogen peroxide.

$$H_2SO_5+H_2O_2 \rightarrow H_2SO_4+H_2O+O_2$$

3. On distilling with dilute H_2SO_4 it forms hydrogen peroxide.

$$H_2SO_5+H_2O \xrightarrow{H_2SO_4} H_2O_2+H_2SO_4$$

It is a powerful *oxidising agent* even more than *perdisulphuric acid.* It oxidises halogen acids to halogens.

$$\begin{array}{l} H_2SO_5 \rightarrow H_2SO_4+\text{'}O\text{'} \\ 2HX+\text{'}O\text{'} \rightarrow H_2O+X_2 \\ \hline 2HX+H_2SO_5 \rightarrow H_2O+X_2+H_2SO_4 \; (X=Cl,\, Br,\, I) \end{array}$$

Similarly, it liberates halogen from halides. Iodine is liberated almost immediately.

$$\begin{array}{c} H_2SO_5 \rightarrow H_2SO_4 + \text{'}O\text{'} \\ 2KI + H_2SO_4 \rightarrow K_2SO_4 + 2HI \\ 2HI + \text{'}O\text{'} \rightarrow H_2O + I_2 \\ \hline 2KI + H_2SO_5 \rightarrow I_2 + K_2SO_4 + H_2O \end{array}$$

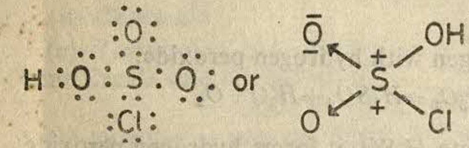
It oxidises aniline into aniline black. The acid has got no action on $KMnO_4$.

Uses : It is used as strong oxidising agents.

9.10. Some Electronic Structures of Sulphur Compounds

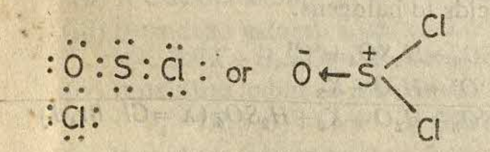
(i) *Sulphuryl chloride* : SO_2Cl_2. The total number of valency electrons available in the molecule are 32 (six for sulphur and oxygen atoms and seven for each chlorine atom). The total number of atoms is 5. All the atoms having the complete separate octets would require $5 \times 8 = 40$ electrons. The number of bonds is thus $\frac{1}{2}(40-32)=4$. This is compatible with the semi polar bond structures.

(ii) *Chlorosulphonic acid* : The number of valency electrons available $= 7+24+1=32$. For five atoms Cl, S and $3O$, the octets are complete, if these are $5 \times 8 = 40$ electrons, and for one hydrogen atom the duet is complete with two electrons, i.e. in all $40+2=42$ electrons are required for separate octets. The number of bonds is, therefore, $\frac{1}{2}(42-32)=5$, and this agrees with the structures represented below :



(iii) *Sulphur dioxide*, $SO_2 \rightarrow$ See SO_2.

(iv) *Thionyl chloride*, $SOCl_2$: The number of valency electrons $=6+6+7+7=26$, the complete separate octets demand 32 electrons for 4 atoms. Therefore, the number of bonds is $\frac{1}{2}(32-26)=3$.



(v) *Sulphurous acid*, H_2SO_3 : The number of valency electron $=2+6+6\times 3=26$, two hydrogen atoms require $2 \times 2 = 4$ electrons and 4 atoms of S and $3O$ require 32 electrons for individual complete octets. Therefore, the number of bonds is are

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9.10.

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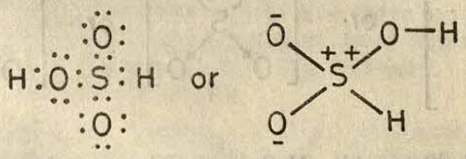
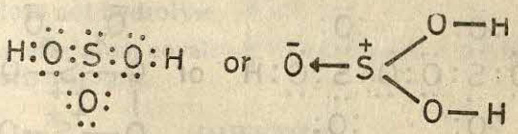
$\frac{1}{2}(36-26)=5$. The symmetrical and unsymmetrical structures are shown below :

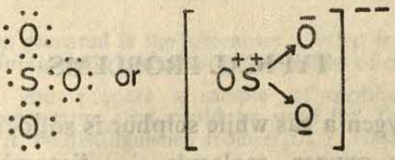
(a) Symmetrical :



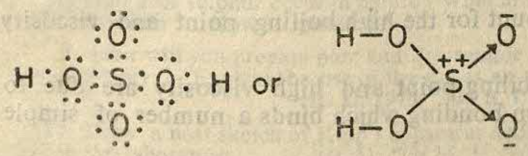
(b) Unsymmetrical :

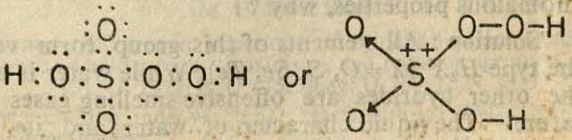


(vi) *Sulphur trioxide*, SO_3. The number of valency electrons is 24. The four atoms require 32 electrons for complete octets. The number of bonds is $\frac{1}{2}(32-24)=4$.

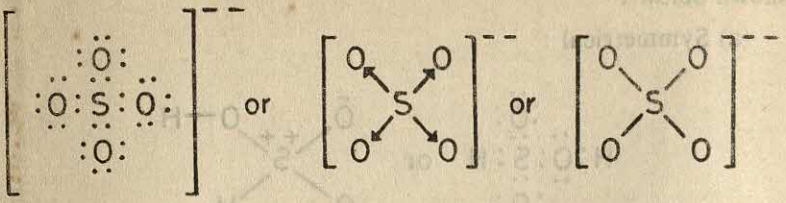


(vii) *Sulphuric Acid*, H_2SO_4. The number of valency electrons is 32, for complete octets, we require $4+40=44$ electrons. The number of bonds is, thus $\frac{1}{2}(44-32)=6$.

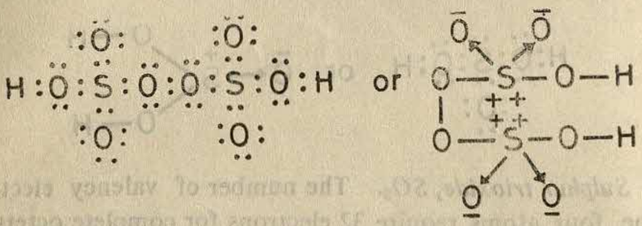




The sulphate ion (SO_4) can be shown as follows :



(viii) *Marshall's acid*, $H_2S_2O_8$: The number of bonds are $\frac{1}{2}(84-62)=11$.



(ix) *Caro's acid*, H_2SO_5 : The number of bonds are $\frac{1}{2}(52-38)=7$.

TYPICAL PROBLEMS

1. Why is oxygen a gas while sulphur is solid ?

Solution : The oxygen molecule is diatomic. Under normal conditions oxygen exists as a gas. The molecules of other elements have larger atomocities and they exist as solids. Thus, sulphur has 8 atoms per molecule which are arranged in the form of puckered ring as shown in the structure of sulphur. Hence it exists as solid.

2. How do you account for the high boiling point and viscosity of sulphuric acid ?

Solution : Its high boiling point and high viscosity are due to the presence of hydrogen bonding which binds a number of simple molecules into clusters.

3. Among the hydrides of oxygen family elements, water shows anomalous properties, why ?

Solution : All elements of this group form volatile hydrides of the type H_2X ($X=O, S, Se, Te$). While water is an odourless liquid, the other hydrides are offensive smelling gases at ordinary temperature. The liquid character of water and its other anomalous properties are due to hydrogen bonding in it.

4. The tendency to show the -2 oxidation state diminishes from sulphur to polonium, why ?

Solution : Oxygen exhibits the -2 oxidation state the electronegativities of the other elements are much less. Hence, there is a very low probability for them to form dinegative ions. The tendency for the -2 oxidation state diminishes from sulphur downwards. This is reflected in the instability of the hydrides. The hydride of polonium, H_2Po is very unstable.

5. Why elements of VIA (O_2, S, and Se) are known as chalcogens ?

Solution : They are referred to as chalcogens (ore forming elements) because many common ores of metals are either oxides or sulphides.

6. SF_6 does not hydrolyse, why ?

Ans. The maximum covalency of sulphur is 6 which is satisfied with six fluorine atoms.

QUESTION

Long Type Questions :

1. Discuss the position of oxygen, sulphur, selenium, tellurium and polonium in the periodic table.

2. Outline the chief points of similarity and dissimilarity between oxygen and sulphur.

3. How is oxygen prepared in the laboratory ? What is the function of MnO_2 in this reaction ? Mention three anomalous properties of oxygen.

4. How would you prepare a sample of ozonised oxygen ? Draw a neat sketch of the apparatus that could be used for the purpose. Give its properties. How can it be distinguished from H_2O_2 ? (Bhag. U. 1975, R. U. '65)

5. (a) Describe one method of preparing ozone in the laboratory.

(b) Explain one method of ascertaining the formula of ozone.

6. Describe the preparation, properties and uses of ozone.

7. Describe the preparation and properties of the allotropic modification of sulphur. How would you prove that these are chemically idention ?

8. How does sulphur occur in nature ? What are the Gill and Frasch processes of its extraction ? How is purified ?

9. How will you prepare pure and dry sample of hydrogen sulphide gas in the laboratory ? Explain the use of the gas as an analytical reagent.
(R. U. 1970, '73; B. U. '73; M. U. '67; Bhag. U. '67)

10. Draw a neat sketch of Kipp's apparatus and describe its use in preparing H_2S in the laboratory. (P. U. '73; M. U. '80, '81; Bhag. U. '80; BIEC '83)

11. Illustrate how hydrogen sulphide acts as a (a) reducing agent, (b) dibasic acid. (M. U. 1967; Bhag. U. '74; R. U. '68, '70)

12. Describe how you would prepare a specimen of sulphur dioxide. Discuss the reaction of sulphur dioxide both as oxidising and reducing agent. Give equations. (M. U. 1975; B. U. '75; Bhag. U. '68; L. N. M. U. '76)

13. Write down the condition under which SO_2 reacts with (a) HNO_3, (b) H_2S, (c) bromine and (d) sodium iodate.

14. How can sulphur dioxide be converted into sulphur trioxide and then into sulphuric acid ? What procedure would you adopt in diluting concentrated sulphuric acid and why ? Illustrate the use of sulphuric acid as (a) a dehydrating agent, (b) an oxidising agent. **(P. U. 1968; B. U. '69, 82; R. U. '75; Bhag. U. '78; M. U. 69; L. N. M. U. '75; Bhag. U. '80)**

15. Describe the manufacture of sulphuric acid by chamber process. What are the functions of Glover and Gay Lussac's tower in a sulphuric acid plant ? What experiments may be performed to illustrate these reactions ?

Sulphurie acid may act as (a) an oxidising agent, (b) a dibasic acid. **(R. U 1975; M. U. '79; P. U. '74)**

16. Describe the principles involved in the manufacture of sulphuric acid by contact process. What is the oxidation number of sulphur in sulphuric acid ? How does it react with carbon and phosphorus ?

17. A. Coloured element reacts with conc. H_2SO_4 to give coloured solution, B. and colourless gas, C. the solution B gives black precipitate, D. with H_2S and deep blue solution, E. with excess of NH_4OH solution. The gas C gives yellow precipitate F with H_2S, the precipitate F is soluble in CS_2 and gives pungent smell when burnt in air. Identify A, B, C, D, E and F and write down the reaction,

18. Salt A reacts with dil. HCl to give gas B and solution C. The gas B has got rotten egg smell and it gives black precipitate D with lead aectate solution. The solution C gives white precipitate E with $AgNO_3$ solution which is soluble in excess of ammonia giving F. Identify A, B, C, D, E and F.

19. How will you distinguish between :

(a) CO_2 and SO_2
(b) SO_2 and H_2S
(c) Na_2CO_3 and Na_2S
(d) Na_2CO_3 and Na_2SO_3
(e) Na_2S and Na_2SO_4
(f) Na_2SO_3 and Na_2SO_4
(g) $CuSO_4$ and $NiSO_4$
(h) $ZnSO_4$ and $HgSO_4$
(i) $CuSO_4$ and $ZnSO_4$
(j) $PbCl_2$ and $MnCl_2$
(k) $Cu(NO_3)_2$ and $CO\ (NO_3)_2$?

20. Explain the following :

(i) Oxygen is a gas but sulphur is a solid.

(ii) Oxygen shows only divalency, the other members of the group show valencies of 4 and 6 also.

(iii) The boiling point and viscosity of H_2SO_4 is very high.

(iv) The tendency to show −2 oxidation state diminishes from sulphur to polonium.

(v) H_2O is a liquid but H_2S is a gas.

(vi) H_2S is not prepared by the action of conc. H_2SO_4 on iron pyrite or FeS.

(vii) Conc. H_2SO_4 is a dehydrating agent.

(viii) Conc. H_2SO_4 is a desiccating agent.

(ix) H_2SO_4 is always an oxidising agent.

(x) SO_2 is an acidic gas.

(xi) SO_2 is an oxidising agent.

(xii) SO_2 is a reducing agent.

(xiii) SO_2 is a bleaching agent.

(xiv) CO_2 can be obtained by passing SO_2 to Na_2CO_3 solution.

(xv) HI is not prepared by the action of conc. H_2SO_4 on sodium or potassium iodide (or metal lodides).

(xvi) H_2S is not desiccated by (a) CaO, (b) conc. H_2SO_4, (c) $ZnCl_2$.

(xvii) H_2S can be used to distinguish between $CuSO_4$ and $NiSO_4$ solution.

21. What are the principal types of reaction of sulphuric acid ? Illustrate your answer by suitable examples of each type. **(P. U. 1974; B. U. '63; M. U. '67)**

Short Type Questions :

22. What happens when hydrogen sulphide is passed through—

(a) copper sulphate solution acidified with hydrochloric acid ?
(b) zinc sulphate solution made alkaline with ammonium hydroxide solution in the presence of ammonium chloride ?
(c) ammonium hydroxide solution ?
(d) iodine suspended in water ?
(e) ferric chloride solution ? **(Bhag. U. 1974; P. U. '63; M. U. '63)**
(f) dil. Nitric acid ? **(R. U. 1964; B. U. '63; Bhag. U. '74)**
(g) conc. H_2SO_4 ? **(Bhag. U. '1970)**
(h) acidified potassium permanganate solution ? **(Bhag. U. 1974; B. U. '71)**
(i) acidified potassium dichromate solution ? **(R. U. 1969; M. U. '80; Bhag. U. '81)**
(j) sulphur dioxide ? **(Bhag. U. '80)**
(k) hydrogen peroxide ?
(l) lead acetate ? **(B. U. 1971)**
(m) mercuric chloride ? **(M. U. 1980)**
(n) caustic soda ? **(B U. 1963; P. U. '57)**

Give equations where necessary.

23. What happens when sulphur dioxide is passed through

(a) chlorine or bromine water ? **(R. U. 1967)**
(b) potassium permanganate solution (acidified) ? **(P. U. 1975; Bhag. U. '63; R. U. '75)**
(c) acidified potassium dichromate solution ? **(R. U. 1967; P. U. '75)**
(d) sodium carbonate solution ? **(B. U. 1966)**
(e) alkaline potassium permanganate solution ?
(f) nitric acid ? **(R. U. 1964)**
(g) Hydrogen sulphide ?
(h) sodium iodate solution ? **(R. U. 1964)**
(i) magnesium ? **(R. U. 1975)**
(j) $FeCl_3$ solution ? **(R. U. 1966)**

Select and write the correct answer :

24. A salt of sulphurous acid is called
(1) sulphite, (2) sulphate, (3) sulphide, (4) thiosulphate.

25. Which of the following burns to form an oxide which is gaseous at room temperarure ?
(1) H_2, (2) He, (3) Na, (4) S.

26. Which one of the following is true peroxide ?
(1) NO_2, (2) BaO_2, MnO_2 (4) SO_2.

27. When SO_2 is passed through acidified $N_2Cr_2O_7$
(1) the solution turns blue.
(2) the solution is decolourised.
(3) green $Cr_2(SO_4)_3$ is formed.
(4) SO_2 is reduced.

28. When H_2S is passed through acidified $KMnO_4$, we get
(1) K_2SO_3, (2) MnO_2, (3) S, (4) $KHSO_3$.

29. Lead chamber is used for the manufacture of :
(1) Nitric oxide, (2) Ammonia, (3) Bleaching Powder, (4) Sulphuric acid.

30. When SO_2 is passed through acidified solution of H_2S
(1) H_2SO_3 is formed,
(2) sulphur is precipitated,

(3) H_2SO_4 is formed,
(4) $H_2S_2O_7$ is formed.

31. Which of the following acid acts as dehydrating and desiccating agent?
(1) H_2SO_3, (2) H_2SO_4, (3) $H_2S_2O_7$, (4) $H_2S_2O_8$.

32. Which of the following acid is used in wet battery ?
(1) HNO_3, (2) HNO_2, (3) H_2SO_3, (4) H_2SO_4.

33. H_2SO_4 is manufactured by lead chamber process, the catalyst used is
(1) finely divided iron,
(2) finely divided nickel,
(3) oxides of nitrogen,
(4) oxides of vanadium.

34. SO_2 is incombustible and non-supporter of combustion but strongly burning potassium or magnesium continues to burn in a jar of the gas
(1) because K or Mg have affinity for SO_2,
(2) because K or Mg have low ignition point,
(3) because the heat of the reaction is enough to dissociate the gas into S and free oxygen,
(4) because K or Mg have high molecular energy.

35. CO_2 and SO_2 can be distinguished by
(1) Lime water, (2) Baryta water,
(8) $NaOH$, (4) $K_2Cr_2O_7$ solution.

36. Bleaching action of SO_2 is due to
(1) oxidation, (2) reduction,
(3) hydrogen, (4) its acidic nature.

37. Which of the following gives black precipitate with H_2S in dil. HCl medium ?

(1) $NiSO_4$ soln, (2) $ZnSO_4$ soln, (3) $CuSO_4$ soln, (4) $MnSO_4$ soln.

38. 11·2 litres of SO_2 reacts with 11·2 litres of H_2S under the same condition of temp. and pressure then the weight of sulphur obtained is

(1) 96 gm, (2) 48 gm, (3) 24 gm, (4) 12 gm.

39. When SO_2 is passed into acidified $K_2Cr_2O_7$ solution then change in oxidation state of chromium is from

(1) 6 to -2, (2) $+2$ to -6, (3) $+3$ to $+6$, (4) $+6$ to $+3$.

40. Which of the following gases are obtained when a mixture of $NaCl$ and NaI is heated with conc. H_2SO_4 ?

(1) HCl, HI, (2) HCl, I_2, (3) Cl_2, I_2, SO_2, (4) HCl, SO_2, I_2.

41. Hydrogen chloride is obtained by heating $NaCl$ and conc. H_2SO_4. This is because :

(1) conc. H_2SO_4 is stronger than hydrochloric acid,
(2) hydrogen chloride is a gas whereas H_2SO_4 is a liquid,
(3) sulphates are more soluble than chlorides,
(4) sulphates are less soluble than chlorides.

42. Which of the following is insouble in water ?

(1) Na_2SO_4, (2) K_2SO_4, (3) $CuSO_4$, (4) $BaSO_4$.

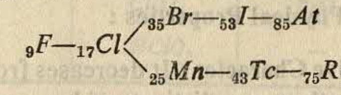
□□□

CHAPTER 10

STUDY OF THE ELEMENTS OF HALOGEN FAMILY

Introduction :

Group VII of periodic table consists of 8 elements. These elements are divided into two sub-groups VIIA and VIIB. The family relationships of this group are shown below :



$$_{9}F-{}_{17}Cl \begin{cases} {}_{35}Br-{}_{53}I-{}_{85}At \\ {}_{25}Mn-{}_{43}Tc-{}_{75}Re \end{cases}$$

The sub-group A contains fluorine, chlorine, bromine and iodine, a closely related family of elements, known as *halogens*. All of these are p-block elements. All of these are normal elements. There are seven electrons (ns^2np^5) in the outermost shell of the elements. These elements show a marked resemblance and possess a regular gradation in their properties. It justifies their inclusion in the same group of the periodic table.

Element	*At. No.*	*Electronic configuration*	*At. Radius* Å	*Electro-negativity*	*Electron affinity*	*First I.P.* eV	*Density*
F	9	$[He]\ 2s^22p^5$	0·72	4·0	3·74	17·42	1·1
Cl	17	$[Ne]\ 3s^23p^5$	0·99	3·0	4·02	13·01	1·57
Br	35	$[Ar]\ 3d^{10}4s^24p^5$	1·14	2·8	3·78	11·84	3·14
I	53	$[Kr]\ 4d^{10}5s^25p^5$	1·33	2·4	3·44	10·44	4·94

Position in the Periodic Table :

SIMILARITY

1. **Electronic configuration** : They all possess seven electrons in their outermost orbit (see table).

2. **Molecular state :** They all form diatomic molecules.

3. (a) **Mono Electrovalency** : Being short of one electron that a saturated structure, they readily react with alkali metals which possess an easily detachable electron in the outermost orbit and are thus monovalent in electrovalent compounds.

(b) All are non-metallic on account of high electronegativity. All are diatomic molecule. Since Vander Waal's forces between these discrete atoms are weak so they are volatile in nature. Volatility decreases with increase of At. No.

(c) Halogen molecules are coloured (due to absorption of visible light). F absorbs violet light (high energy) and I absorbs yellow light (lower energy). Thus they are yellow and violet respectively.

Gradual Change in Physical Properties :

1. **Electro-negative Character** : It decreases from fluorine to iodine. However, in iodine there are distinct evidences of some electro +ve behaviour in the formation of iodine phosphate, iodine acetate and iodine perchlorate. The metallic lustre is an instance of this behaviour. Iodine forms iodine monochloride by loss of an electron which is characteristic of metals.

2. (a) **Physical constant** : Size of the atom, atomic weight, density, melting point and boiling point, atomic radius, atomic volume increase with rise in atomic number.

	F	Cl	Br	I
At. Wt.	19	35·5	80	127
Density	1·3	1·9	3·4	4·93
M.P.	−233°	−102°	−70°	+114°
B.P.	−178°	−34°	59°	184°

3. **Colour**: Fluorine and chlorine are pale yellow and greenish yellow gases, bromine is dark red liquid and iodine is violet solid.

4. **Stability** : The stability of their molecules X_2 decrease with increase of at. wt. Thus at 1200°C while fluorine is not dissociated at all, chlorine is slightly dissociated, bromine is dissociated to the extent of 6%, iodine is highly dissociated.

5. **I. P. and electronegativity** : It decreases with rise in atomic number (see table).

6. **Bond energy** : It is low in fluorine molecules (due to repulsion between non-bonding electrons) while in Cl_2, Br_2, I_2 its value is high. Thus bond energy increases from fluorine to iodine.

7. Oxidation states : They have got the following oxidation states.

Oxidation No.	*Fluorine*	*Chlorine*	*Bromine*	*Iodine*
−1	HF	HCl	HBr	HI
0	F_2	Cl_2	Br_2	I_2
+1	—	$HOCl$	$HOBr$	HOI
+3	—	$HClO_2$	$HBrO_2$	—
+4	—	ClO_2	BrO_2	I_2O_4
+5	—	$HClO_3$	$HBrO_3$	HIO_3
+6	—	Cl_2O_6	BrO_3	—
+7	—	$HClO_4$	—	HIO_4

Gradual Change in Chemical Properties :

1. Reactivity : It is very reactive. It reacts with metals as well as with many non-metals. Its reactivity decreases with rise in at. no. Fluorine is highly reactive because of low energy of $F—F$ bond, small size of atoms or ions, high electronegativity and also due to very powerful oxidising power.

2. Combination with H_2 : All combine with hydrogen to form acids but the reactivity decreases from fluorine to iodine. Fluorine reacts in dark, chlorine reacts in sunlight, bromine reacts on heating, while iodine reacts only in the presence of a catalyst.

3. Reaction with H_2O : The reactivity with water decrease from fluorine to iodine. Fluorine reacts with H_2O violently in dark, chlorine and bromine react with water in sunlight while iodine does not react at all.

4. Oxidising action : It decreases from fluorine to iodine. Fluorine is a powerful oxidising agent while iodine is a mild one.

$$F_2+H_2O\rightarrow 2F^-+2H^++\tfrac{1}{2}O_2 \ \Delta G=-190 \text{ K cal./mole}$$
$$I_2+H_2O\rightleftharpoons 2I^{-1}+\tfrac{1}{2}O_2+2H^+ \ \Delta G=+25 \text{ K cal./mole}$$

5. Displacement reactions : It decreases with rise in atomic number. Fluorine displaces all other halogens from their salts while iodine cannot do so at all.

$$2KCl+F_2\rightarrow 2KF+Cl_2$$
$$2KBr+F_2\rightarrow 2KF+Br_2$$
$$2KI+F_2\rightarrow X$$

6. Activity of Hydracids : It increases from H_2F_2 to HI. H_2F_2 is very stable and not easily oxidised, HCl is oxidised by MnO_2 and

$KMnO_4$ and HBr and HI are easily oxidised and hence act as strong reducing agents. H_2F_2 and HCl are very stable; HBr suffers slight dissociation at 1000°C while HI dissociates appreciably at 400°C.

7. **Oxy-Acids** : All the halogen elements excepting Fluorine form oxyacids. The stability of acids increases from chlorine to iodine.

8. **Reaction with O_2** : In oxide fluorine exhibits oxidation state of -1 and -2 while the oxides of Cl, Br, I have oxidation state from $+1$ to $+7$, examples of oxides are F_2O, Cl_2O, Br_2O, ClO_2, BrO_2, ClO_3, BrO_3, etc. All form oxyacids except fluorine.

9. **Formation of interhalogen compounds** : The halogens combine with each other to form interhalogen compounds.

This similarity and gradation in their properties justifies the inclusion of all the four halogens in the same group of the periodic table.

Summary :

(1) The properties which **decrease from Fluorine to Iodine** (F_2 to I_2) :

(a) Electronegativity, (b) Ionization potential, (c) Electronegativity, (d) Electron affinity Cl, F, Br, I, (e) Oxidising property, (f) Reactivity, (g) Acidic nature, (h) Covalent nature.

(2) The properties which **increase from Fluorine to Iodine** (F_2 to I_2) :

(a) Atomic size, (b) Metallic nature, (c) Electropositive nature (d) Reducing property, (e) Basic nature, (f) Solid nature, (g) Lattice energy.

10.1. Fluorine

Symbol F At. No. 9 At. Wt. 19·4

Electronic Configuration $1s^2 2s^2 2p_x^2 p_y^2 p_z^1$

Occurrence :

Fluorine is a highly reactive element and occurs only in the combined state. Some of the important minerals which contain fluroine are :

(i) Fluorspar, CaF_2, (ii) Cryolite, Na_3AlF_6 or $3NaF.AlF_3$,

(iii) Fluorapatite $CaF_2.Ca_3(PO_4)_2$.

It is also present in small quantities in sea water, in plants and in teeth and bones of animals.

Methods of Preparation :

The following reasons resulted in a considerable delay in the isolation of fluorine—

(i) Fluorine is a highly reactive element and reacts with most of the elements.

(ii) It attacks the common materials of construction of apparatus such as glass, rubber and metals.

(iii) Anhydrous hydrofluoric acid is poisonous, a poor conductor of electricity and corrosive in nature.

(iv) An aqueous solution of hydrofluoric acid on electrolysis gives hydrogen at cathode and oxygen at anode.

Preparation : The preparation of fluorine has been a very difficult problem in chemistry. In spite of the repeated attempts, the gas could not be prepared as it was so reactive that the electrons or vessel used in the process were attacked. The various methods that have been employed are :

(i) Moisson's Method (1886) :

The essential parts of the apparatus used are

Electrolyte .. Anhydrous liquid hydrofluoric acid+20%KHF_2

Electrodes .. *Pt-Ir* alloy

Vessel .. *Pt-Ir*; U-tube cooled to −23°C by keeping immersed in a bath of methyl chloride (B.P. −23°C)

On electrolysis fluorine is liberated at anode. The method is however, no longer in use as it involved a loss of about 6 gm of platinum for one gm of fluorine produced.

(ii) Denni's Method (1931) :

The apparatus consists of

Electrolyte .. Pure and dry KHF_2 (m.p. 722)

Electrodes .. Graphite rods.

The fig. 10·1 is shown below.

The electrolytic cell consists of V-shaped copper tube fitted with copper caps into which are cemented graphite electrodes. The cell is covered with an insulation layer of asbestos cement over which is wound a resistance wire for electrical heating so as to keep electrolytes in fused state. The whole cell is covered by a lagging to prevent loss of heat by radiation.

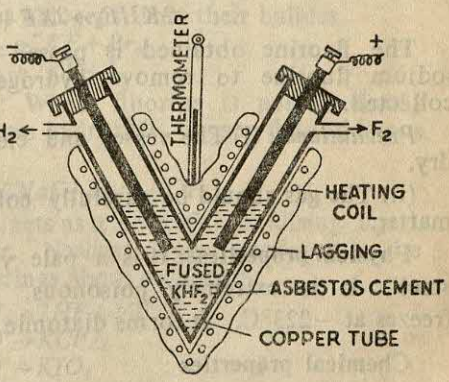


Fig. 10·1. Denni's method

Reactions :

$$KHF_2 \rightarrow KF + HF$$
$$HF \rightarrow H^+ + F^-$$

The reaction of the cathode is :

$$2H^+ + 2e \rightarrow H_2$$

and the reaction at the anode is :

$$2F^- \rightarrow F_2 + 2e$$

Disadvantages : (i) Fluorine formed in this method is unable to escape out sufficiently fast due to narrow exist round anode and hence frothing of electrolyte is produced which further prevents the escape of fluorine.

(ii) H_2 and F_2 get mixed up and hence cause explosion.

(iii) Denbigh and Whitlaw Gray's method (1934) :

This is the modern method for the preparation of fluorine. In this method fused KHF_2 is electrolysed in an electrically heated copper cell which also serves as cathode. A graphite rod surrounded by a copper diaphragm perforated at the bottom is used as an anode. The diaphragm prevents the mixing of hydrogen and fluorine which, if allowed would react explosively. On passing the electric current hydrogen and fluorine are evolved at the cathode and anode respectively.

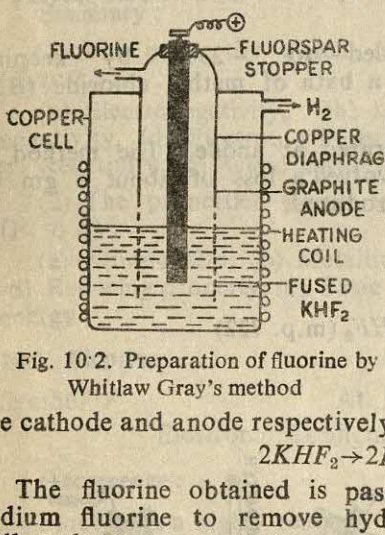


Fig. 10·2. Preparation of fluorine by Whitlaw Gray's method

$$2KHF_2 \rightarrow 2KF + H_2 + F_2$$

The fluorine obtained is passed through U-tubes containing sodium fluorine to remove hydrogen fluoride vapours and is collected.

Precautions : (i) The vessel and electrolyte must be absolutely dry.

(ii) The gas should be carefully collected as it attacks organic matter.

Physical properties : It is a pale yellow gas with an irritating smell. It is extremely poisonous. It liquifies at −187°C and freezes at −223°C. It forms diatomic molecule, F_2.

Chemical properties :

As fluorine is the most electronegative element, it combines directly with all other elements except nitrogen, oxygen and the noble gases. Some important reactions are given below :

(a) *Reaction with Hydrogen and water* : Fluorine has a great affinity for hydrogen. It combines with moist hydrogen with explosive violence in the dark and even at −252°C

$$H_2+F_2 \rightarrow 2HF(g)+128 \text{ Kcal}$$

It fumes in moist air : It decomposes water producing ozonised oxygen and hydrogen fluoride.

$$2H_2O+2F_2 \rightarrow 4HF+O_2$$
$$3H_2O+3F_2 \rightarrow 6HF+O_3$$

(b) *Reaction with metals* : Fluorine reacts with metals forming fluorides.

(i) Spontaneous reaction :

$$2Na+F_2 \rightarrow 2NaF; \quad Ca+F_2 \rightarrow CaF_2$$

(ii) On slight heating :

$$2Ag+F_2 \rightarrow 2AgF; \quad Mg+F_2 \rightarrow MgF_2$$

(iii) At 300°C :

$$2Au+3F_2 \rightarrow 2AuF_3; \quad Pt+2F_2 \rightarrow PtF_4$$

(c) *Reaction with non-metals* :

(i) $S+3F_2 \rightarrow SF_6$ (Sulphur hexafluoride)

(ii) $P_4+10F_2 \rightarrow 4PF_5$ (Phosphorus pentafluoride)

(d) *Reaction with Metalloids* : Metalloids, such as arsenic and antimony burn spontaneously in fluorine forming fluorides.

$$3As+3F_2 \rightarrow 2AsF_3$$
$$2Sb+3F_2 \rightarrow 2SbF_3$$

(e) *Reaction with hydrogen compounds* : Hydrogen fluoride is produced in each case.

$$H_2S+4F_2 \rightarrow 2HF+SF_6$$
$$CH_4+4F_2 \rightarrow 4HF+CF_4$$

(f) *Reaction with Halides* : Since fluorine is the most electronegative elements, it displaces other halogens from their halides.

$$2KBr+F_2 \rightarrow 2KF+Br_2$$
$$2KI+F_2 \rightarrow 2KF+I_2$$

(g) *Reaction with alkalies* : When fluorine is passed slowly through a dilute solution of sodium hydroxide, oxygen difluoride gas is produced.

$$2NaOH+2F_2 \rightarrow 2NaF+H_2O+OF_2$$

(h) *As an oxidising agent* : It acts as a powerful oxidising agent in the presence of traces of water. Nascent oxygen produced by the reaction of fluorine with water brings about oxidation.

$$H_2O+F_2 \rightarrow 2HF+\text{'}O\text{'}$$
$$KClO_3+\text{'}O\text{'} \rightarrow KClO_4$$
$$KIO_3+\text{'}O\text{'} \rightarrow KIO_4$$

Uses : (i) It is used as a rocket fuel.

(ii) It is used for making fluorides.

(iii) It is used in the manufacture of Uranium hexafluoride.

(iv) It is used for making polytetra fluoriethylene ($CF_2=CF_2$) (*PTFE*) which shows exceptional resistance to solvents and boiling acids including aqua regia.

10.2. Chlorine (Cl)

Atomic number—17 Atomic weight—35·5

Electronic configuration : $1s^2 2s^2 2p^6 3s^2 3p^5$

Occurrence :

Chlorine does not occur in the free state in nature. Sodium chloride is the richest source of chlorine. Sylvine, KCl and carnallite, $KCl\ Mg\ Cl_2\ fH_2O$ are the other chlorides which occur in nature.

Methods of Preparation :

Chlorine is prepared by the action of oxidising agent on concentrated hydrochloric acid as given below :

(a) Manganese dioxide :

$$MnO_2+4HCl\xrightarrow{\text{heat}}MnCl_2+Cl_2+2H_2O$$

(b) Potassium permangate (In cold condition) :

$$\begin{array}{c}
2KMnO_4\rightarrow K_2O+2MnO+5\text{'}O\text{'}\\
K_2O+2HCl\rightarrow 2KCl+H_2O\\
2MnO+4HCl\rightarrow 2MnCl_2+2H_2O\\
10HCl+5\text{'}O\text{'}\rightarrow 5H_2O+5Cl_2\\
\hline
2KMnO_4+16HCl\rightarrow 2KCl+2MnCl_2+5Cl_2+8H_2O
\end{array}$$

$$[2MnO_4^{-1}+16H^{+}+10Cl^{-}\rightarrow 5Cl_2+2Mn^{+2}+8H_2O]$$

(c) Potassium dichromate (In cold condition) :

$$\begin{array}{c}
K_2Cr_2O_7\rightarrow K_2O+Cr_2O_3+3\text{'}O\text{'}\\
K_2O+2HCl\rightarrow 2KCl+H_2O\\
Cr_2O_3+6HCl\rightarrow 2CrCl_3+3H_2O\\
6HCl+3\text{'}O\text{'}\rightarrow 3H_2O+3Cl_2\\
\hline
K_2Cr_2O_7+14HCl\rightarrow 2KCl+2CrCl_3+3Cl_2+7H_2O
\end{array}$$

$$[Cr_2O_7^{-2}+14H^{+}+6Cl^{-}\rightarrow 3Cl_2+2Cr^{+3}+7H_2O]$$

(d) Lead dioxide (Heat) :

$$\begin{array}{c}
PbO_2\rightarrow PbO+\text{'}O\text{'}\\
PbO+2HCl\rightarrow PbCl_2+H_2O\\
2HCl+\text{'}O\text{'}\rightarrow H_2O+Cl_2\\
\hline
PbO_2+4HCl\rightarrow PbCl_2+Cl_2+2H_2O
\end{array}$$

(e) Red lead (Heat) :

$$Pb_3O_4+8HCl\rightarrow 3PbCl_2+4H_2O+Cl_2$$

(f) Bleaching Powder (Cold) :

$$\begin{array}{c}
Ca(OCl)Cl\rightarrow CaCl_2+\text{'}O\text{'}\\
2HCl+\text{'}O\text{'}\rightarrow H_2O+Cl_2\\
\hline
Ca(OCl)Cl+2HCl\rightarrow CaCl_2+Cl_2+H_2O
\end{array}$$

(g) Hydrogen peroxide (Cold):

$$H_2O_2+2HCl\rightarrow 2H_2O+Cl_2$$

$$(O_2^{-2}+4H^{+}+2Cl^{-}\rightarrow 2H_2O+Cl_2)$$

Laboratory Preparation : (a) *From manganese dioxide* :

Principle : Chlorine is prepared in the laboratory by heating a mixture of manganese dioxide and common salt with conc. H_2SO_4 in a flask.

$$\begin{array}{c} NaCl+H_2SO_4\rightarrow NaHSO_4+HCl\ [\times 2] \\ MnO_2+H_2SO_4\rightarrow MnSO_4+H_2O+\text{`}O\text{'} \\ 2HCl+\text{`}O\text{'}\rightarrow H_2O+Cl_2 \\ \hline 2NaCl+3H_2SO_4+MnO_2\rightarrow 2NaHSO_4+MnSO_4+2H_2O+Cl_2 \end{array}$$

Note : This is general method for the preparation of bromine, iodine etc. $NaBr$ or NaI is taken in place of $NaCl$.

$$2NaX+3H_2SO_4+MnO_2\xrightarrow{\text{heat}}2NaHSO_4+MnSO_4+2H_2O+X_2$$

$$(X=Cl,\ Br,\ I)$$

Description : A mixture of manganese dioxide and common salt is taken in the round bottomed flask. Conc. H_2SO_4 is added through the thistle funnel till the end of it sufficiently below the acid in the flask (Fig. 10.3). The flask is carefully heated on a sand bath, then greenish yellow vapours of chlorine are evolved.

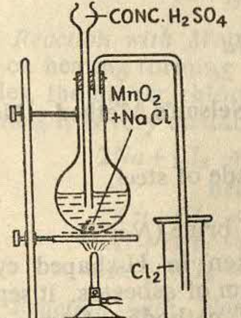


Fig. 10.3. Laboratory preparation of chlorine

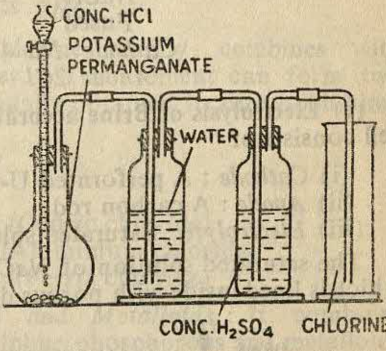


Fig. 10.4. Pure and dry chlorine

Collection : It is collected by the upward displacement of air ($D_{air}=14{\cdot}4$, $D_{Cl_2}=35{\cdot}5$) since it is heavier than air and soluble in water.

(b) *From Potassium Permanganate* : Chlorine can also be obtained in the laboratory by dropping conc. HCl on powdered Potassium Permanganate. The fig. 10.4 indicates the preparation of pure and dry chlorine.

$$2KMnO_4+16HCl\rightarrow 2KCl+2MnCl_2+5Cl_2+8H_2O$$

Purification and Drying : It contains water vapours and hydrochloric acid as impurities.

(a) It is bubbled through water to remove hydrochloric acid.

(b) It is passed through conc. H_2SO_4 to remove moisture.

Industrial Preparation : Chlorine is prepared industrially by the following process :

(a) **Deacon's Process** : HCl gas can be oxidised to give chlorine by heating a mixture of HCl gas and air at 400°C–450°C in the presence of cupric chloride. The reaction is exothermic.

$$4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2 + 28 \text{ Kcal (exothermic)}$$

The HCl is obtained by heating a mixture of $NaCl$ and conc. H_2SO_4. The mixture of HCl gas and air is preheated in a chamber to about 200°C. This heated mixture is then led into the catalyst chamber. The catalyst chamber contains pieces of burnt clay and cupric chloride ($CuCl_2$). The purity of chlorine obtained by this method is not very high. This is mostly used in the manufacture of bleaching powder.

(b) **Down Process (Electrolysis of Fused Sodium Chloride)** : Chlorine is obtained as a bye-product in the extraction of sodium from sodium chloride. In this case sodium chloride is fused and electrolysed by using Iron as cathode and graphite as anode then chlorine is evolved at anode.

$$\underset{\text{Fused}}{NaCl} \overset{\text{Electrolysis}}{\rightleftharpoons} Na^+ + Cl^-$$

$$\text{Cathode } Na + e \rightarrow Na$$

$$\text{Anode } 2Cl \rightarrow Cl_2 + 2e$$

(c) **Electrolysis of Brine according to Nelson's Method** : Nelson's cell consists of

(i) *Cathode* : A perforated U-tube made of steel,
(ii) *Anode* : A carbon rod.
(iii) *Electrolyte* : Saturated solution of brine ($NaCl$).

The saturated solution of $NaCl$ is taken in U-shaped cylinder which is lined inside with porous diaphragm of asbestos. It separates cathode from anode. The carbon rod is dipped in sodium chloride solution.

The whole of this cell is suspended in an iron tank.

On passing the current, chlorine is evolved at the anode and is collected. The sodium ion passes through the asbestos and changes to sodium atom at the

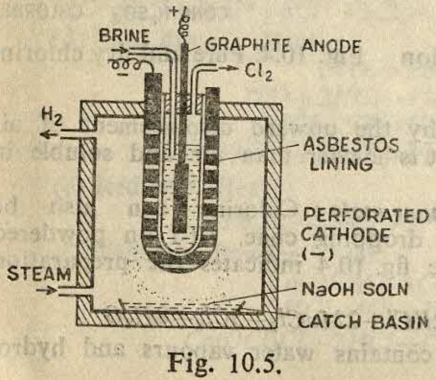


Fig. 10.5.

cathode. It reacts with steam to form caustic soda and hydrogen gas.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

At the cathode : $2H_2O + 2e \rightarrow H_2 + 2OH^-$

$$Na^+ + OH^- \rightleftharpoons NaOH$$

At the anode : $Cl^- \rightarrow Cl + e$

$$Cl + Cl \rightarrow Cl_2$$

Physical Properties : (a) Chlorine is a greenish yellow gas with a suffocating smell. (b) It is soluble in water and the solution on cooling forms chlorine hydrate ($Cl_2.8H_2O$) at 0°C. (c) It is about 2½ times heavier than air. (d) Chlorine has three isotopes of atomic masses—35, 37 and 39. (e) On cooling under pressure it is liquefied to a yellow liquid (b. p. $-34{\cdot}06$°C); on further cooling, it freezes to give a pale yellow solid (m.p. -101°C).

Chemical Properties :

Since it is a highly electronegative element, hence it is very active but is less active than fluorine.

(a) *Reaction with Hydrogen* : It combines directly but slowly in the dark forming hydrogen chloride.

$$H_2 + Cl_2 \rightarrow 2HCl$$

(b) *Reaction with Metals* : Chlorine readily combines with metals on heating forming chlorides. If an element can form two chlorides, the higher chloride is usually obtained by direct combination unless it is very unstable.

$$2Na + Cl_2 \rightarrow 2NaCl$$

$$Cu + Cl_2 \xrightarrow{\text{heat}} CuCl_2 \text{ (Cupric chloride)}$$

$$Al + 3Cl_2 \rightarrow AlCl_3 \text{ (Aluminium chloride)}$$

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3 \text{ (Ferric chloride)}$$

(c) *Reaction with Non-Metals and Metalloids* : It combines readily with non-metals such as sulphur, phosphorous and metalloids such as arsenic and antimony. Some of these elements spontaneously catch fire in an atmosphere of chlorine.

$$S_8 \text{ (boiled)} + 4Cl_2(g) \rightarrow 4S_2Cl_2 \text{ (Sulphur chloride)}$$

$$P_4 + 10Cl_2 \rightarrow 4PCl_5 \text{ (Phoshorus Penta chloride)}$$

$$2Sb + 3Cl_2 \rightarrow 2SbCl_3 \text{ (Antimony trichloride)}$$

(d) *Reaction with Alkalies* : (MOH, $M = Na$, K)

(i) Chlorine reacts with a cold dilute alkali solution to form a mixture of a *chloride* and a *hypochlorite* :

$$\begin{array}{l} Cl_2 + H_2O \rightarrow HCl + HClO \\ MOH + HCl \rightarrow MCl + H_2O \\ MOH + HOCl \rightarrow MClO + H_2O \\ \hline 2MOH + Cl_2 \rightarrow MCl + MClO + H_2O \end{array}$$

(ii) Chlorine reacts with a hot dilute alkali solution to form a mixture of a *chloride* and a *chlorate* is obtained.

$$\begin{array}{rcl} 2MOH+Cl_2 & \rightarrow & MCl+MClO+H_2O\ [\times 3] \\ 3MClO & \rightarrow & MClO_3+2MCl \\ \hline 6MOH+3Cl_2 & \rightarrow & MClO_3+5MCl+3H_2O \\ & & (M=Na,\ K) \end{array}$$

(e) *Reaction with* $Ca(OH)_2$:

(i) Cold condition :

$$2Ca(OH)_2+2Cl_2 \rightarrow CaCl_2+\underset{\text{Cal. hypochlorite}}{Ca(OCl)_2}+2H_2O$$

(ii) Hot condition :

$$6Ca(OH)_2+6Cl_2 \rightarrow 5CaCl_2+\underset{\text{Cal. chlorate}}{Ca(ClO_3)_2}+6H_2O$$

(iii) At 40°C :

$$Ca(OH)_2+Cl_2 \rightarrow \underset{\text{Bleaching powder}}{Ca(OCl)Cl}+H_2O$$

(f) *Reaction with Ammonia* :

(i) *Excess of* NH_3 *and little* Cl_2 ; When chlorine reacts with excess of ammonia, nitrogen is evolved and ammonium chloride is produced :

$$\begin{array}{rcl} 2NH_3+3Cl_2 & \rightarrow & N_2+6HCl \\ 6NH_3+6HCl & \rightarrow & 6NH_4Cl \\ \hline 8NH_3+3Cl_2 & \rightarrow & N_2+6NH_4Cl \end{array}$$

(ii) *Little of* NH_3 *and Excess* Cl_2 : When ammonia reacts with excess of chlorine, nitrogen trichloride is formed. Nitrogen trichloride is an explosive substance in the dry state.

$$NH_3+3Cl_2 \rightarrow NCl_3+3HCl$$

(g) *As an Oxidising Agent* : Since it gains electrons during a chemical reaction, hence it acts as an oxidising agent.

$$Cl_2+2e \rightarrow 2Cl^{-1}$$

In the presence of moisture it produces atomic oxygen which brings about the oxidation of many substances.

(i) Hydrogen sulphide to sulphur :

$$H_2S+\underbrace{Cl_2 \rightarrow 2HCl}_{\underset{\text{Reduced}}{OA}}+S$$

(ii) Sulphur dioxide to sulphuric acid :

$$\begin{array}{rcl} H_2O+Cl_2 & \rightarrow & 2HCl+\text{'}O\text{'} \\ SO_2+\text{'}O\text{'}+H_2O & \rightarrow & H_2SO_4 \\ \hline SO_2+Cl_2+2H_2O & \rightarrow & H_2SO_4+2HCl \end{array}$$

(iii) Nitrites to Nitrates :

$$\begin{array}{rcl} H_2O+Cl_2 & \rightarrow & 2HCl+\text{'}O\text{'} \\ NaNO_2+\text{'}O\text{'} & \rightarrow & NaNO_3 \\ \hline NaNO+Cl_2+H_2O & \rightarrow & NaNO_3+2HCl \\ \text{Sod. Nitrite} & & \text{Sod. Nitrate} \end{array}$$

(iv) Arsenites to Arsenates :

$$\begin{array}{rcl} H_2O+Cl_2 & \rightarrow & 2HCl+\text{'}O\text{'} \\ Na_3AsO_3+\text{'}O\text{'} & \rightarrow & Na_3AsO_4 \\ \hline Na_3AsO_3+Cl_2+H_2O & \rightarrow & Na_3AsO_4+2HCl \end{array}$$

(v) Sulphites and Thiosulphates to Sulphates :

$$\begin{array}{rcl} H_2O+Cl_2 & \rightarrow & 2HCl+\text{'}O\text{'} \\ Na_2SO_3+\text{'}O\text{'} & \rightarrow & Na_2SO_4 \\ \hline Na_2SO_3+H_2O+Cl_2 & \rightarrow & Na_2SO_4+2HCl \\ \text{Sod. Sulphite} & & \text{Sod. Sulphate} \end{array}$$

$$\begin{array}{rcl} H_2O+Cl_2 & \rightarrow & 2HCl+\text{'}O\text{'} \\ Na_2S_2O_3+\text{'}O\text{'} & \rightarrow & Na_2SO_4+S \\ \hline Na_2S_2O_3+H_2O+Cl_2 & \rightarrow & Na_2SO_4+2HCl+S\downarrow \\ \text{Sod. Thiosulphate} & & \text{Sod. Sulphate} \end{array}$$

(vi) Ferrous salt to Ferric salts :

(a) $$2FeCl_2+Cl_2 \rightarrow 2FeCl_3$$

(b) $$\underset{\text{Ferrous Sulphate}}{2FeSO_4}+H_2SO_4+Cl_2 \rightarrow \underset{\text{Ferric Sulphate}}{Fe_2(SO_4)_3}+2HCl$$

(vii) Mercurous salts to Mercuric salts :

$$Hg_2Cl_2+Cl_2 \rightarrow 2HgCl_2$$

(viii) Stannous salts to Stannic salts :

$$SnCl_2+Cl_2 \rightarrow SnCl_4$$

(h) *Formation of Addition compounds* : Chlorine forms addition compounds with many unsaturated compounds such as carbon monoxide, sulphur dioxide, ethylene and acetylene etc.

$CO+Cl_2 \rightarrow COCl_2$ (Phosgene, Carbonyl Chloride)
$SO_2+Cl_2 \rightarrow SO_2Cl_2$ (Sulphuryl Chloride)
$C_2H_2+2Cl_2 \rightarrow C_2H_2Cl_4$ (Acetylene Tetrachloride)

(*i*) *Substitution reactions* : It substitutes hydrogen from hydrocarbons forming substitution products e.g. methane (CH_4) forms methyl chloride, methylene chloride, chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4) :

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl;\ CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$
$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl;\ CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$

(j) *Reaction with Halides* : Chlorine replaces Bromine or Iodine from bromides and iodides because it is more electronegative than Bromine and Iodine.

$$2KBr + Cl_2 \rightarrow 2KCl + Br_2$$
$$2KI + Cl_2 \rightarrow 2KCl + I_2$$

(k) *As a Bleaching Agent* : Chlorine acts as a powerful bleaching agent in the presence of moisture due to the formation of atomic oxygen. The atomic oxygen oxidises coloured compounds to a colourless product. Bleaching by chlorine is permanent and the colour does not reappear on standing.

$$Cl_2 + H_2O \rightarrow 2HCl + \text{'O'}$$

$$\text{Coloured substance} + \text{'O'} \rightarrow \text{Colourless} \xrightarrow[\text{From air}]{\text{'O'}} \text{Colourless (permanent).}$$

(l) *As Germicide* : It acts as a disinfectant and a germicide as the atomic oxygen kills harmful bacteria and germs.

Tests : (i) It turns moist starch iodide paper blue and bleached.

$$\begin{array}{l} \text{Starch} \\ \text{iodide} \\ \text{paper} \end{array} \left[\begin{array}{l} 2KI + Cl_2 \rightarrow 2KCl + I_2 \\ \text{Starch} + I_2 \rightarrow \text{Blue} \xrightarrow{Cl_2} \text{Bleached.} \end{array} \right.$$

(2) It bleaches moist litmus paper.

(3) It is a greenish yellow gas with a pungent smell.

Uses : Chlorine is used :

(a) as a bleaching agent in the manufacture of rayon, paper, linen and cotton textiles.

(b) for the manufacture of poisonous gases such as phosphene, mustard gas and tear gas.

(c) in the manufacture of dyes, explosives and synthetic rubber.

(d) for the manufacture of bleaching powder, $Ca(OCl)Cl$.

(e) for sterilisation of drinking water.

Summary

1. By the action of HCl → on oxidising agent
   $MnO_2+4HCl\rightarrow Cl_2+MnCl_2+2H_2O$
2. $2KMnO_4+16HCl\rightarrow 5Cl_2+2KCl+2MnCl_2+8H_2O$ →
3. $H_2O_2+2HCl\rightarrow 2H_2O+Cl_2$ →
4. $K_2Cr_2O_7+14HCl\rightarrow 3Cl_2+2KCl+2CrCl_3+7H_2O$ →
5. $PbO_2+4HCl\rightarrow PbCl_2+Cl_2+2H_2O$ →
6. Deacon's Process →
   $HCl+\text{'}O\text{'}\xrightarrow{CuCl_2}H_2O+Cl_2$
7. Down Process → Electrolysis of fused $NaCl$
8. Nelson Process → Electrolysis of fused $NaOH$

Chlorine

Greenish yellow gas, Acidic

O.A. Bleaching Agent

$+H_2$ → HCl

P_4 → PCl_5

Metal → Metal Chloride

$NaOH$ → (a) Cold : $NaCl+NaClO+H_2O$
(b) Hot : $NaCl+NaClO_3+H_2O$

NH_3 → Little Cl_2 → N_2+NH_4Cl
Excess Cl_2 → NCl_3+HCl

As O.A. → in aqueous medium.

(a) $NaNO_2+H_2O+Cl_2\rightarrow NaNO_3+2HCl$

(b) $Na_2SO_3+H_2O+Cl_2\rightarrow Na_2SO_4+2HCl$

(c) $Na_3AsO_3+H_2O+Cl_2\rightarrow Na_3AsO_4+2HCl$

(d) $SO_2+Cl_2+2H_2O+Cl_2\rightarrow H_2SO_4+2HCl$

(e) $2FeSO_4+H_2SO_4+Cl_2\rightarrow Fe_2(SO_4)_3+2HCl$

As Bleaching Agent → It bleaches due to nascent 'O' and permanent.

10.3. BROMINE (Br)

Atomic Number : 35 Atomic weight : 80

Electronic configuration : $1s^22s^22p^63s^23p^63d^{10}4s^24p^5$

Occurrence :

It occurs in nature only in the combined state. Carnallite, $KCl.MgCl_2.6H_2O$ contains about 1% of potassium and magnesium bromides. Bromides of sodium, potassium and magnesium are also present in sea water.

Laboratory Preparation :

Principle : Bromine is prepared in the laboratory by heating a mixture of manganese dioxide and potassium bromide with conc. H_2SO_4 in a flask.

$$\begin{aligned} KBr+H_2SO_4 &\rightarrow KHSO_4+HBr\ [\times 2] \\ MnO_2+H_2SO_4 &\rightarrow MnSO_4+H_2O+\text{'O'} \\ 2HBr+\text{'O'} &\rightarrow H_2O+Br_2 \\ \hline 2KBr+MnO_2+3H_2SO_4 &\rightarrow 2KHSO_4+MnSO_4+2H_2O+Br_2 \end{aligned}$$

Description : A mixture of mangnese dioxide, potassium bromide and conc. H_2SO_4 is taken in a retort (fig. 10.6) and heated. Reddish brown vapours of bromine are evolved and are condensed in the receiver which is being cooled by tap water.

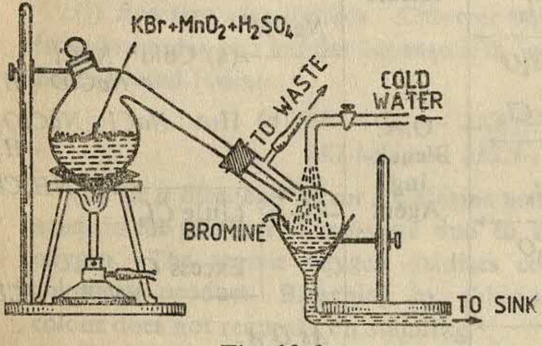


Fig. 10.6.

Industrial Preparation :

The carnallite $KCl.MgCl_2.6H_2O$ contains about 1% of potassium and magnesium bromides. The mother liquor left behind after the crystallisation of $KCl.MgCl_2.6H_2O$ contains these bromides.

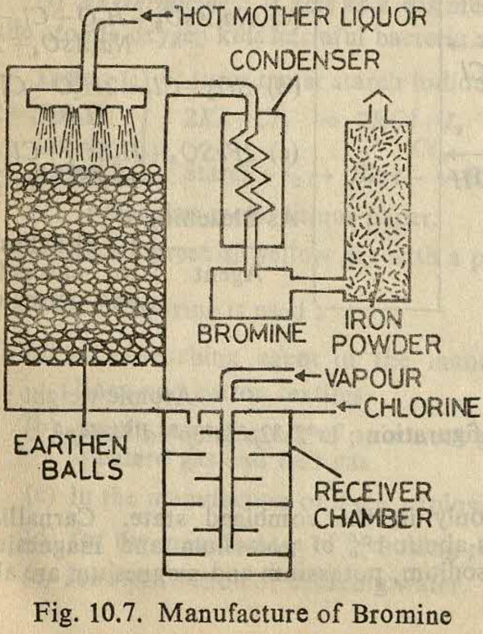


Fig. 10.7. Manufacture of Bromine

The hot mother liquor is allowed to come down as a fine spray from the top of a tower packed with earthen ware balls (Fig. 10.7). A current of chlorine enters the tower through an inlet near the bottom and comes in contact with the hot mother liquor. Vapours of bromine are liberated and come out of the tower near the top. These are led into cooling chamber where they are cooled by water and condense to give a reddish brown liquid.

Reactions : $2KBr + Cl_2 \rightarrow 2KCl + Br_2$

$$MgBr_2 + Cl_2 \rightarrow MgCl_2 + Br_2$$

Collection : The uncondensed vapours of bromine are passed through a tower packed with moist iron filings. These are absorbed by iron filing due to the formation of ferric bromide. This is subsequently treated for the recovery of bromine.

$$3Fe + 4Br_2 \rightarrow Fe_3Br_8$$

Purification : The commercial bromine contains small amounts of chlorine, iodine and water as impurities. It is distilled with a mixture of potassium bromide and zinc oxide. Potassium bromide removes chlorine and zinc oxide removes Iodine and concentrated sulphuric acid removes moisture:

$$2KBr + Cl_2 \rightarrow 2KCl + Br_2$$
$$2ZnO + I_2 \rightarrow 2ZnI_2 + O_2$$

Physical Properties :

(i) It is a dark red heavy liquid having a specific gravity of 3.12.

(ii) It gives out irritating vapour and produces sores on the skin.

(iii) It is fairly soluble in water. The reddish brown solution is known as bromine water which on cooling deposits crystals of $Br_2.10H_2O$.

(iv) Its b.p. is 58·8°C but forms a brown solid at −7°C.

Chemical Properties :

Bromine is also chemically a very active element but less than fluorine and chlorine. Most of the reactions of bromine are similar to those of chlorine.

(a) *Reaction with Hydrogen* : Bromine combines with hydrogen on heating forming hydrogen bromide.

$$H_2 + Br_2 \rightarrow 2HBr$$

(b) *Reaction with non-metals and Metalloids* : Bromine combines with a number of non-metals such as phosphorus (P), Boron (B) and silicon (Si) and metalloids, such as Arsenic (As) and Antimony (Sb) to form their bromides.

$$P_4 + 6Br_2\text{ (vap.)} \rightarrow 4PBr_3\text{ (Burns)}$$
$$2As + 3Br_2\text{ (vap.)} \rightarrow 2AsBr_3\text{ (Burns)}$$
$$2Sb + 3Br_2\text{ (vap.)} \rightarrow 2SbBr_3\text{ (Burns)}$$
$$2B + 3Br_2 \xrightarrow{\text{heat}} 2BBr_3$$

(c) *Reaction with metals* : Bromine combines with a number of metals to form bromides.

$$2Na + Br_2 \rightarrow 2NaBr$$
$$2Al + 3Br_2 \rightarrow 2AlBr_3$$

Laboratory Prepapation :

(a) It can be prepared in the laboratory by heating a mixture of potassium iodide and manganese dioxide with concentrated sulphuric acid in a beaker (Fig. 10.8), vapours of iodine are formed which on cooling, form the crystals of iodine.

$$2KI + MnO_2 + 3H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + 2H_2O + I_2$$

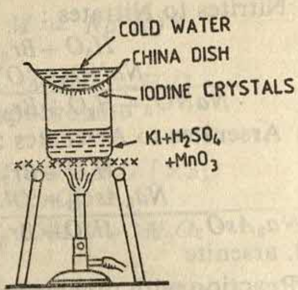


Fig. 10.8

(b) By the action of chlorine or bromine with potassium iodide solution.

$$2KI + Cl_2 \rightarrow 2KCl + I_2$$
$$2KI + Br_2 \rightarrow 2KBr + I_2$$

Industrial Preparation : Iodine is prepared on an industrial scale from sea weeds and from caliche (crude chile salt petre)

(a) *From sea weeds* (Laminaria—0·4-1·5% I_2 as impurity) :

(i) Sea weeds especially of the laminaria variety are collected, dried and burnt in shallow pits to avoid loss of iodine. The ash obtained is known as kelp. It contains 0·4-1·5% Iodine besides chlorides and sulphates of sodium and potassium.

(ii) The chlorides and sulphates of alkali metals are separated by fractional crystallisation. The mother liquor contains NaI.

(iii) The mother liquor is heated with manganese dioxide and concentrated sulphuric acid. The heating is done in a cast iron retort filled with a lead cover and connected to stone-ware receivers called aludels. The iodine produced undergoes sublimation and condenses in the aludels from where it is collected (Fig. 10.9).

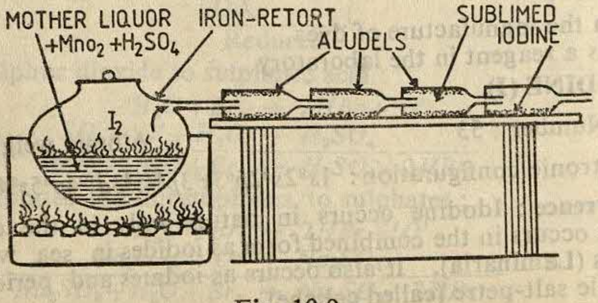


Fig. 10.9

Summary :

$$\text{Sea Weeds} \xrightarrow[\text{2. Burnt}]{\text{1. Dried}} \text{Ash (Kelp)} \xrightarrow[\text{2. Filter}]{\text{1. Laxiviated with water}} \text{Filtrate}$$

$$\text{Filtrate} \xrightarrow{\text{Crystallise}} NaI \xrightarrow[\text{heat}]{+Mn+H_2SO_4} I_2 \text{ (Sublimes)}$$

(b) *From Caliche* : (crude chile salt petre) Caliche or crude chile salt petre in addition to sodium nitrate contains 0·5% Sodium iodate $NaIO_3$. The solution is concentrated and cooled when sodium nitrate crystallises out while sodium iodate remains in the mother liquor. This is treated with sodium bisulphite solution when sodium iodate is reduced to iodine which precipitates out. This is filtered and purified by sublimation.

$$\begin{aligned} NaIO_3+3NaHSO_3 &\rightarrow NaI+3NaHSO_4\ [\times 5] \\ NaHSO_4+NaI &\rightarrow Na_2SO_4+HI\ [\times 5] \\ NaHSO_4+NaIO_3 &\rightarrow Na_2SO_4+HIO_3 \\ HIO_3+5HI &\rightarrow 3H_2O+3I_2 \\ \hline 6NaIO_3+15NaHSO_3 &\rightarrow 6Na_2SO_4+9NaHSO_4+3H_2O+3I_2 \end{aligned}$$

or $$2NaIO_3+5NaHSO_3 \rightarrow 2Na_2SO_4+3NaHSO_4+H_2O+I_2$$

Purification : The commercial iodine contains small amounts of iodine chloride (ICl) and iodine bromide (IBr). These impurities can be removed by heating it with KI in an iron retort when iodine sublimes over and is collected.

$$KI+ICl \rightarrow KCl+I_2\uparrow;\ KI+IBr \rightarrow KBr+I_2\uparrow$$

Physical Properties :

(a) Iodine is a blackish grey crystalline solid with a metallic lustre.

(b) It is volatile at ordinary temperature and sublimes on heating to give violet coloured vapours having a pungent and irritating smell.

(c) On careful heating, it melts at 114°C. Its boiling point is 184°C.

(d) It is very slightly soluble in water. The solution is brown in colour. It is readily soluble in a solution of KI due to the formation of potassium tri-iodide. This solution behaves as a simple mixture of potassium iodide and iodine.

$$KI+I_2 \rightarrow KI_3 \text{ (Pot. tri-iodide)}$$

Iodine is readily soluble in most of the organic solvents. Its solution in CS_2, $CHCl_3$ or CCl_4 is violet in colour while its solution in ether or alcohol is brown.

Chemical Properties :

Iodine resembles chlorine and bromine in its chemical properties but it is less active than either of them.

1. *Reaction with Hydrogen* : Iodine has little affinity for hydrogen. It combines with it only on heating in the presence of a catalyst.

$$H_2+I_2 \xrightleftharpoons{Pt\ 400^\circ C} 2HI$$

Unlike other halogens, iodine *does not react with water*.

2. *Reaction with metals* : Iodine reacts directly with a number of metals to form metal iodides.

$$2K+I_2 \rightarrow 2KI \text{ (Vigorous reaction)}$$
$$Hg+I_2 \rightarrow HgI_2 \text{ (On heating)}$$

3. *Reaction with Non-Metals and Metalloids* : Non-metals like Phosphorus and metalloids such as arsenic and antimony combine directly with iodine vapours to form iodides.

$$P_4+6I_2 \rightarrow 4PI_3 \text{ (Phosphorus tri-iodide)}$$
$$2As+3I_2 \rightarrow 2AsI_3 \text{ (Arsenic tri-iodide)}$$

4. *Reaction with Alkalies* : $(M=Na, K)$: Iodine reacts with a cold and dilute alkali solution to give a solution containing an iodide and hypo-iodous acid. Hypo iodite formed in the first instance is hydrolysed by water forming hypoiodous acid.

$$MOH+I_2 \rightarrow MI+MIO+H_2O$$
$$\underline{MIO+H_2O \rightarrow (HIO+MOH}$$
$$MOH+I_2 \rightarrow MI+HIO \text{ (Hypoidous acid)}$$

It reacts with a hot and concentrated alkali solution to give a mixture of Potassium iodide and Potassium iodate.

$$2KOH+I_2 \rightarrow KI+KIO+H_2O\ [\times 3]$$
$$\underline{3KIO \rightarrow 2KI+KIO_3}$$
$$6KOH+3I_2 \rightarrow KIO_3+5KI+3H_2O$$

5. *Reaction with Ammonia* : It reacts with liquid ammonia to form nitrogen tri-iodide.

$$2NH_3+3I_2 \rightarrow NI_3.NH_3+3HI$$

Nitrogen tri-iodide behaves as explosive in the dry state. Vapours of iodine are liberated when it explodes.

$$8NH_3.NI_3 \rightarrow 6NH_4I+9I_2+5N_2$$

6. *As an Oxidising Agent* : Iodine acts as an oxidising agent in the presence of moisture although it is not as powerful as other members of the halogen family.

$$I_2+2e \rightarrow 2I^{-1} \text{ (Gains elecrons, o.a.)}$$

It oxidises—

(i) Hydrogen sulphide to sulphur :

$$I_2+H_2S \rightarrow 2HI+S$$
$$(I_2+S^{-2} \rightarrow 2I^-+S)$$

(ii) Sulphur dioxide to sulphuric acid :

$$SO_2+2H_2O+I_2 \rightarrow H_2SO_4+2HI$$
$$(SO_2+2H_2O+I_2 \rightarrow SO_4^{-2}+2I^-+4H^+)$$

(iii) Sulphites to sulphates :

$$Na_2SO_3+H_2O+I_2 \rightarrow Na_2SO_4+2HI$$
$$(SO_3^{-2}+H_2O+I_2 \rightarrow SO_4^{-2}+2I^-+2H^+)$$

(iv) Sodium thiosulphate to Sodium tetrathionate :

$$2Na_2S_2O_3+I_2 \rightarrow Na_2S_4O_6+2NaI$$
$$(2S_2O_3^{-2}+I_2 \rightarrow S_4O_6^{-2}+2I^-)$$

(v) Arsenites to Arsenates :

$$Na_3AsO_3+H_2O+I_2 \rightarrow Na_3AsO_4+2HI$$
$$(AsO_3^{-3}+H_2A+I_2 \rightarrow AsO_4^{-3}+2I^{-1}+2H^+)$$

(vi) Nitrites to Nitrates :

$$NaNO_2+H_2O+I_2 \rightarrow NaNO_3+2HI$$
$$(NO_2^{-1}+H_2O+I_2 \rightarrow NO_3^{-1}+2I^-+2H^+)$$

7. *Reaction with HNO_3* : Conc. HNO_3 oxidises moist Iodine to iodic acid. In this reaction Iodine acts as reducing agent.

$$2HNO_3 \rightarrow H_2O+2NO_2+\text{'}O\text{'}\ [\times 5]$$
$$\underline{I_2+5\text{'}O\text{'}+H_2O \rightarrow 2HIO_3}$$
$$I_2+10HNO_3 \rightarrow 2HIO_3+10NO_2+4H_2O$$

8. *Reaction with Potassium chlorate* : It forms potassium iodate and chlorine when it is heated with a concentrated solution of potassium chlorate containing a little nitric acid.

$$2KClO_3+I_2 \rightarrow 2KIO_3+Cl_2$$

9. *Reaction with chlorine* : It reacts with chlorine in aqueous-medium to give iodic acid (HIO_3). In this reaction iodine acts as a reducing agent.

$$I_2+5Cl_2+6H_2O \rightarrow 2HIO_3+10HCl$$

10. *Reaction with chlorine* : Dry Cl_2 and dry iodine combine to give iodine monochloride.

$$I_2+Cl_2 \rightleftharpoons 2ICl$$

11. *As a germicide* : Iodine destroys germs and is therefore, used as a disinfectant and an analgesic in the form of tincture iodine. It is not a bleaching agent.

12. *Reaction with starch :* It turns a freshly prepared starch solution or moist starch paper blue.

13. *Dissociation :* The dissociation starts at about 700°C and is complete at about 1700°C. Its vapour is violet.

$$I_2 \rightleftharpoons 2I$$

14. *Reaction with sulphur dioxide :* When SO_2 is passed into iodine it is reduced to hydroiodic acid.

$$I_2+SO_2+2H_2O \rightarrow H_2SO_4+2HI$$

Tests : Iodine is detected by the following tests.

(a) Its vapours are violet in colour.

(b) It turns a freshly prepared starch solution or moist starch paper blue.

Uses : Iodine is used :

(a) As a disinfectant. Tinctured iodine is an important disinfectant prepared by dissolving iodine in potassium iodide solution and diluting this solution with alcohol.

(b) In the manufacture of iodoform, iodole and iodex. Silver iodide is used in photography. Iodole acts as an antiseptic and iodex is used as an analgesic.

(c) As a reagent in the laboratory.

(d) In the treatment of goitre.

10.4. Comparison of the Properties of Halogens

Properties	*Chorine*	*Bromine*	*Iodine*
1. Atomic structure	2, 8, 7	2, 8, 18, 7	2, 8, 18, 18, 7
2. E. C.	$\boxed{Ne}\ 3s^23p^5$	$\boxed{Ar}\ 3d^{10}4s^24p^5$	$\boxed{Kr}\ 4d^{10}5s^25p^5$
3. Valency	1	1	1
4. Atomic number	17	35	53
5. Atomic weight	35·5	80	127
6. Physical state	Gas	Liquid	Solid
7. Colour	Greenish yellow	Dark brown liquid, reddish brown vapours	Dark grey solid, violet vapours
8. Smell	Irritating	More so	Intensely so
9. Density g.c.c.	1·51 (liq.)	3·12 (liq.)	4·92 (solid)
10. General activity	Very active	Less active	Least active
11. Reaction with H_2 $H_2+X_2 \rightarrow 2HX$	Reacts in sunlight	Reacts on heating	Reacts in presence of a catalyst

Properties	*Chlorine*	*Bromine*	*Iodine*
12. Reaction with H_2O	Reacts slowly forming HCl and $HClO$ $Cl_2 + H_2O \rightarrow HCl + HClO$	Reacts slowly in the presence of sun light $2Br_2 + 2H_2O \rightarrow 4HBr + O_2$	×
13. Reaction with non-metals	All react except N_2, O_2 and carbon	All react except N_2, Br_2, Si and carbon	Only P_4, As and other halogens react
14. Reaction with metals	Attacks metals less readily	Attacks less readily	Least readily
15. Reaction with other halogens	Displaces bromine and iodine $2KBr + Cl_2 \rightarrow 2KCl + Br_2$ $2KI + Cl_2 \rightarrow 2KCl + I_2$	Displaces iodine only $2KI + Br_2 \rightarrow 2KBr + I_2$	Does not displace any of the halogens
16. Reaction with MOH ($M = Na, K$)	With cold and dilute $Cl_2 + 2MOH \rightarrow MCl + MClO + H_2O$ $(Cl_2 + 2OH^- \rightarrow Cl^- + ClO^{-1} + H_2O)$ With hot and conc. solution $3Cl_2 + 6MOH \rightarrow 5MCl + MClO_3 + 3H_2O$ $(3Cl_2 + 6OH^- \rightarrow 5Cl^{-1} + ClO_3^{-1} + 3H_2O$	With cold and dilute $Br_2 + 2MOH \rightarrow MBr + MBrO + H_2O$ With hot and conc. solution $3Br_2 + 6MOH \rightarrow 5MBr + MBrO_3 + 3H_2O$	With cold and dilute $I_2 + MOH \rightarrow NaI + HIO$ With hot and conc. solution $3I_2 + 6MOH \rightarrow 5MI + MIO_3 + 3H_2O$
17. Oxidising power	Very powerful	Less powerful	Least powerful
18. Bleaching action	Good bleaching agent	Moderate bleaching agent	Does not bleach
19. Oxides and Oxyacids	Forms unstable oxides, Cl_2O, ClO_2, Cl_2O_7 Forms oxy-acids $HClO$, $HClO_3$, $HClO_4$	Forms very unstable oxides Br_2O, Br_2O_2, Br_3O_8. Forms oxy-acids HBr and $HBrO_3$	Forms stable oxides I_2O_4, I_4O_9, I_2O_5. Forms oxy-acids HIO, HIO_3
20. Stability of hydracids	Stable	Unstable, acts as a reducing agent	Least stable, strong reducing agent
21. Stability of oxy-acids	$HClO_3$ least stable. I_2 displaces Cl_2 from $HClO_3$	$HBrO_3$ more stable. I_2 displaces Br_2 from $HBrO_2$	HIO_3 most stable

10.5. Hydrogen Chloride (Hydrochloric Acid)

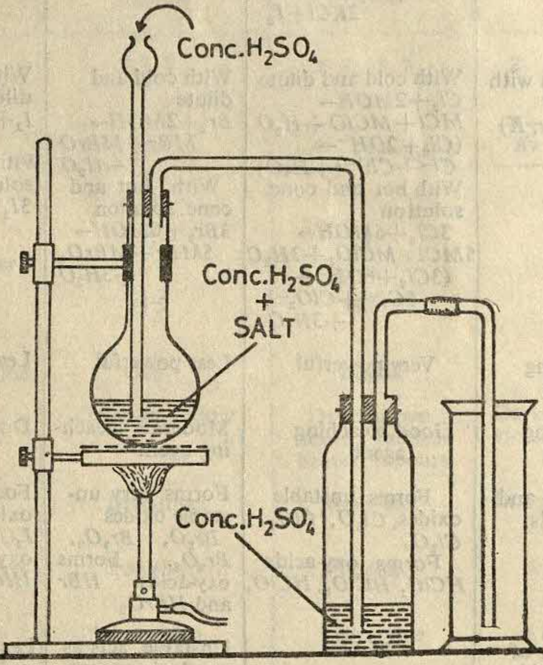
Mol. Formula : HCl Mol. wt. : 36·5

Laboratory Preparation :

(a) Hydrogen chloride gas is prepared in the laboratory by heating sodium chloride with concentrated sulphuric acid.

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + \uparrow HCl$$

Sodium chloride is taken in a round-bottomed flask which is fitted with thistle funnel and a delivery tube. Concentrated sulphuric acid is added through the thistle funnel. On warming the mixture hydrogen chloride gas is evolved and is collected in a dry cylinder by the upward displacement of air. The gas can be dried by bubbling it through concentrated sulphuric acid before it is collected. It cannot be dried by using phosphorus pentoxide or quick lime since it reacts with these compounds.



$$2P_2O_5 + 3HCl \longrightarrow 3HPO_3 + POCl_3$$

Phosphorus pentaoxide Metaphosphoric acid Phosphorus oxychloride

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$$

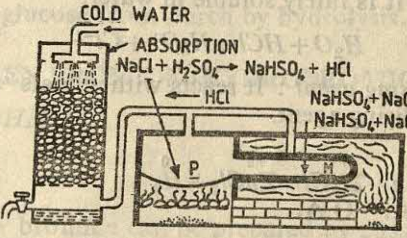
Dissolution of Hydrogen chloride :

Hydrogen chloride gas is highly soluble in water and it it called hydrochloric acid.

(b) *Preparation on large scale* (Manufacture) :

(i) *From common salt* : Common salt as strongly heated with conc. H_2SO_4 in a shallow pan of thick iron to get hydrogen chloride which is absorbed into water to get hydrochloric acid solution. This method, being very expensive, is not much in use

$$NaCl+H_2SO_4 \rightarrow NaHSO_4+HCl$$
$$NaHSO_4+NaCl \rightarrow Na_2SO_4+HCl$$



(ii) *Synthetic Method* : In India and other countries of the world, hydrochloric acid is manufactured by the direct synthesis of hydrogen and chlorine, which are obtained as by-product during the manufacture of caustic soda by the electrolysis of brine.

Physicat Properties : It is a colourless gas with a pungent smell. Its m.p. and b.p. are −111°C and −85°C respectively. It is slightly heavier than air. It is highly soluble in water. It forms a constant boiling mixture containing 22·2% of the acid and boiling at 110°C. A solution of hydrochloric acid cannot, therefore, be concentrated beyond 22·2% by boiling.

Chemical Properties :

(i) *Acidic Properties* : The aqueous solution of hydrogen chloride is called hydrochloric acid. It is strong acid because in water hydrogen chloride dissociates to the extent of about 90 per cent. Hydrochloric acid reacts with most of the metals, such as zinc, magnesium, tin, iron and sodium forming metal chlorides and hydrogen gas. It, however, does not react with silver, gold and platinum.

$$Zn+2HCl \rightarrow ZnCl_2+H_2$$
$$Sn+2HCl \rightarrow SnCl_2+H_2$$

It reacts with oxides and hydroxides of metals to form metal chloride.

$$Al_2O_3+6HCl\rightarrow AlCl_3+3H_2O$$
$$MgO+2HCl\rightarrow MgCl_2+H_2O$$
$$Fe(OH)_3+3HCl\rightarrow FeCl_3+3H_2O$$

It reacts with carbonates, bi-carbonates, sulphides, sulphites, thiosulphates and nitrites. Metal chlorides are produced with evolution of different gases.

$$CaCO_3+2HCl\rightarrow CaCl_2+H_2O+CO_2\uparrow$$
$$NaHCO_3+2HCl\rightarrow NaCl+H_2O+CO_2\uparrow$$
$$Na_2S+2HCl\rightarrow 2NaCl+H_2S\uparrow$$
$$Na_2SO_3+2HCl\rightarrow 2NaCl+H_2O+SO_2\uparrow$$

(b) *Solubility* : It is fairly soluble in water.

$$H_2O+HCl\rightarrow H_3O^{+}+Cl^{-1}$$

(c) *As an oxidising agent* : It reacts with metals showing that it may act as an oxidising agent.

$$\overset{0}{Zn}+2\overset{+1}{H}Cl\rightarrow \overset{+2}{Zn}Cl_2+\overset{0}{H_2}$$

R.A. O.A.

(d) *As a reducing agent* : It acts as a reducing agent in presence of strong oxidising agents such as MnO_2, $KMnO_4$, $K_2Cr_2O_7$, red lead, ozone etc. In all the reactions chlorine is the product.

$$Mn^{+4}O_2+4HCl^{-1}\rightarrow Mn^{+2}Cl_2+Cl_2^{0}+2H_2O$$

O.A. R.A.

$$2KMnO_4+16HCl\rightarrow 2KCl+2Mn^{+2}Cl_2+5Cl_2^{0}+8H_2O$$

O.A. R.A.

$$K_2Cr_2^{+12}O_7+14HCl^{-1}\rightarrow 2KCl+2Cr^{+3}Cl_3+3Cl_2^{0}+7H_2O$$

O.A. R.A.

$$2HCl+O_3\rightarrow H_2O+Cl_2^{0}+O_2$$

R.A O.A.

(e) *Reaction with* (i) *Silver nitrate*, (ii) *Lead acetate*, (iii) *Mercurous nitrate* :

It reacts with $AgNO_3$, $Pb(CH_3COO)_2$ and $Hg_2(NO_3)_2$ solution to give white precipitate of their chlorides.

$$AgNO_3+HCl\rightarrow AgCl\downarrow+HNO_3$$
$$(CH_3COO)_2Pb+2HCl\leftarrow PbCl_2+2CH_3COOH$$
$$Hg_2(NO_3)_2+2HCl\rightarrow Hg_2Cl_2\downarrow+2HNO_3$$

white

(f) *Reaction with Fluorine* : Since fluorine is more electronegative than chlorine, it replaces chlorine from hydrochloric acid.

$$2HCl+F_2\rightarrow 2HF+Cl_2$$

(g) *Formation of Aqua Regia* : A mixture of concentrated hydrochloric acid and concentrated nitric acid in the ratio of 3 : 1 is called *aqua regia.* It dissolves even noble metals like gold and platinum. Atomic chlorine formed by interaction of acids reacts with these metals to form soluble chlorides.

$$3HCl + HNO_3 \rightarrow NOCl + 2\text{'}Cl\text{'} + 2H_2O$$
$$Au + 3\text{'}Cl\text{'} \rightarrow AuCl_3$$

Uses : Hydrochloric acid is used :

(a) as laboratory reagent, (b) in the preparation of Cl_2 and chloride, (c) in the manufacture of dyes and in textile industry, (d) for the extraction of glue from gones, (e) in medicine, (f) in the manufacture of glucose from starch by hydrolysis.

10.6. HYDROGEN BROMIDE (HYDROBROMIC ACID)

Mol. formula : *HBr* Mol. wt. : 81·25

Preparation :

(a) Hydrogen bromide can be prepared by passing a mixture of bromine vapours and hydrogen over an electrically heated platinum spiral.

$$H_2 + Br_2 \rightarrow 2HBr$$

(b) It can also be prepared by heating potassium bromide with phosphoric acid.

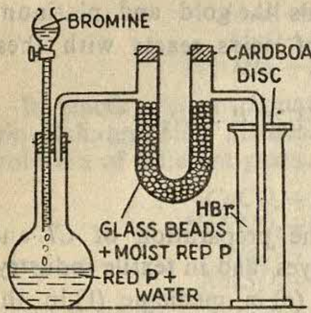
$$3KBr + H_3PO_4 \rightarrow K_3PO_4 + 3HBr$$

Unlike hydrogen chloride it *cannot be prepared by heating a bromide with concentrated sulphuric acid because it reduces sulphuric acid to sulphur dioxide.*

$$\begin{array}{l} 2KBr + H_2SO_4 \rightarrow KHSO_4 + HBr\,(\times 2) \\ \underline{H_2SO_4 + 2HBr \rightarrow SO_2 + Br_2 + 2H_2O} \\ 2KBr + 3H_2SO_4 \rightarrow 2KHSO_4 + SO_2 + Br_2 + 2H_2O \end{array}$$

(c) *Laboratory Preparation* : Hydrogen bromide is prepared in the laboratory by the action of water on phosphorus tribromide. In actual practice, phosphorus is placed in water and bromine is added to it from a dropping funnel. The following reactions take place and hydrogen bromide is produced :

$$P_4 + 6Br_2 \rightarrow 4PBr_3$$
$$PBr_3 + 3H_2O \rightarrow 3HBr + H_3PO_3$$



Lab. preparation of hydrogen bromide

Description : Small pieces of red phosphorus are placed in water contained in a flat-bottomed flask. Liquid bromine is added in small quantities. Vapours of hydrogen bromide are immediately evolved as the reaction is quite fast. These are mixed with a small amount of bromine. These are freed from bromine by passing through a U-tube containing glass beads and moist red phosphorus. Purified hydrogen bromide is finally collected in a dry cylinder by upward displacement of air or dissolved in water to get hydrobromic acid.

Drying of HBr : Hydrogen bromide cannot be dried by passing it through concentrated sulphuric acid because it reduces sulphuric acid to SO_2. Quick lime is also unsuitable for this purpose since hydrogen bromide reacts with it to form calcium bromide.

$$CaO+2HBr \rightarrow CaBr_2+H_2O$$

It can, however, be dried by passing through a U-tube packed with P_2O_5 or anhydrous calcium bromide.

Physical Properties :

(a) It is a colourless gas with pungent smell. (b) It is heavier than air. (c) Its m.p. and b.p. are −86°C and −66·4°C respectively. (d) It is highly soluble in water and hence fumes in moist air.

Chemical Properties :

(a) *Acidic properties* . The solution of hydrogen bromide in water is called hydrobromic acid. It acts as a strong acid and it has a high degree of dissociation.

It reacts with metals such as Mg, Zn, Sn and Fe forming bromides and hydrogen gas.

$$Mg+2HBr \rightarrow MgBr_2+H_2$$

It also reacts with oxides, hydroxides and carbonates of metals to form bromides.

$$MgO+2HBr \rightarrow MgBr_2+H_2O$$
$$NaOH+HBr \rightarrow NaBr+H_2O$$
$$Na_2CO_3+2HBr \rightarrow 2NaBr+H_2O+CO_2\uparrow$$

(b) *Stability and Reducing Properties* : Hydrogen bromide is a relatively unstable compound because its formation is accompanied by evolution of only 8·66 Kcal/mole.

$$H_2+Br_2 \rightarrow 2HBr(g)+17{\cdot}32 \text{ Kcal}$$

On heating to about 800°C, it dissociates to give hydrogen and bromine.

$$2HBr \rightarrow H_2+Br_2$$

Because of its relative stability, it is readily oxidised. Therefore, it acts as a strong reducing agent.

It reduces an acidified solution of potassium permanganate, an acidified solution of potassium dichromate and acidified MnO_2.

(i) $$2KMnO_4+3H_2SO_4 \rightarrow K_2SO_4+2MnSO_4+3H_2O+5`O'$$
$$\underline{2HBr+`O' \rightarrow H_2O+Br_2(\times 5)}$$
$$2KMnO_4+3H_2SO_4+10HBr \rightarrow K_2SO_4+2MnSO_4+8H_2O+5Br_2$$
$$(2MnO_4^-+16H^++10Br^- \rightarrow 2Mn^{+2}+5Br_2+8H_2O)$$

(ii) $$K_2Cr_2O_7+4H_2SO_4 \rightarrow K_2SO_4+Cr_2(SO_4)_3+4H_2O+3`O'$$
$$\underline{2HBr+`O' \rightarrow H_2O+Br_2(\times 3)}$$
$$K_2Cr_2O_7+4H_2SO_4+6HBr \rightarrow K_2SO_4+Cr_2(SO_4)_3+7H_2O+3Br_2$$
$$(Cr_2O_7^{-2}+14H^++6Br^- \rightarrow 2Cr^{+3}+7H_2O+3Br_2)$$

(iii) $$MnO_2+H_2SO_4 \rightarrow MnSO_4+H_2O+`O'$$
$$\underline{2HBr+`O' \rightarrow H_2O+Br_2}$$
$$MnO_2+H_2SO_4+2HBr \rightarrow MnSO_4+2H_2O+Br_2$$
$$(MnO_2+4H^++2HBr^- \rightarrow Mn^{+2}+2H_2O+Br_2)$$

It also reduces H_2SO_4 to SO_2 and HNO_3 to NO_2.

(iv) $$H_2SO_4 \rightarrow H_2O+SO_2+`O'$$
$$\underline{2HBr+`O' \rightarrow H_2O+Br_2}$$
$$2HBr+H_2SO_4 \rightarrow 2H_2O+SO_2+Br_2$$

(v) $$2HNO_3 \rightarrow H_2O+2NO_2+`O'$$
$$\underline{2HBr+`O' \rightarrow H_2O+Br_2}$$
$$2HNO_3+2HBr \rightarrow 2H_2O+2NO_2+Br_2$$

An aqueous solution of hydrobromic acid turns yellow on standing due to its oxidation to bromine by atmospheric oxygen.

(c) *Reaction with silver nitrate* : A pale yellow precipitate of silver bromide is produced when it reacts with a solution of $AgNO_3$.

$$HBr+AgNO_3 \rightarrow AgBr\downarrow+HNO_3$$

(d) *Reaction with halogens* : Fluorine and chlorine being more electronegative than bromine replace it from hydrobromic acid. Iodine being less electronegative has no action.

$$2HBr+F_2 \rightarrow 2HF+Br_2$$
$$2HBr+Cl_2 \rightarrow 2HCl+Br_2$$

Uses : It is used :

(a) as a labratory reagent,
(b) in the preparation of certain bromides.

10.7. HYDROGEN IODIDE (HYDROIODIC ACID)

Mol. Formula : HI Mol. wt : 128·1

Preparation :

(a) Hydrogen iodide can be prepared by passing a mixture of iodine vapours and hydrogen over finely divided platinum at 400°C The combination between the two is only partial as the reaction is reversible.

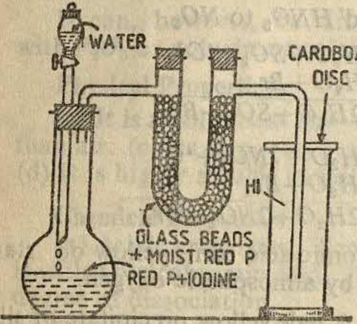
$$H_2+I_2 \rightleftharpoons 2HI$$

(b) It can also be prepared by heating potassium iodide with phosphoric acid.

$$3KI+H_3PO_4 \rightarrow K_3PO_4+3HI$$

Like hydrogen chloride, *it cannot be prepared by heating an iodide with concentrated sulphuric acid because it reduces sulphuric acid to SO_2*.

$$\begin{array}{l} KI+H_2SO_4 \rightarrow KHSO_4+HI\ [\times 2] \\ \underline{H_2SO_4+2HI \rightarrow SO_2+I_2+2H_2O} \\ 2KI+3H_2SO_4 \rightarrow 2KHSO_4+SO_2+I_2+2H_2O \end{array}$$



(c) *Laboratory Preparation :* Hydrogen iodide is prepared in the laboratory by the action of water on phosphorus tri-iodide. In actual practice, a moisture of red phosphorus and iodine is used instead of phosphorus tri-iodide. A mixture of five parts of iodine and one part of red phosphorus is placed in a round-bottomed flask. Water is added dropwise on this mixture from a dropping funnel. The following reactions take place and hydrogen iodide gas is evolved :

$$2P+3I_2 \rightarrow 2PI_3$$
$$PI_3+3H_2O \rightarrow 3HI+H_3PO_3$$

The gas so obtained contains a small quantity of iodine vapours. It is passed through U-tube containing glass beads and moist red phosphorus to remove iodine. The pure gas is collected in a dry cylinder by upward displacement or air, or dissolved in water to get water to get hydriodic acid.

Drying of HI—It is dried by passing the gas through a U-tube packed with P_2O_5 or anhydrous $CaCl_2$.

Conc. H_2SO_4 and quick lime cannot be used for drying it, since it reduces the former to SO_2 and reacts with the latter to form calcium iodide.

$$H_2SO_4+2HI \rightarrow 2H_2O+I_2+SO_2$$
$$CaO+2HI \rightarrow CaI_2+H_2O$$

Physical Properties : (a) It is a colourless gas with pungent smell.

(b) It is heavier than air

(c) Its m.p. and b.p. are −50·8°C and −35·5°C respectively.

(d) It is highly soluble in water and hence fumes in moist air.

Chemical Properties :

(a) *Acidic Properties* : The solution of hydrogen iodide is called hydroiodic acid. It acts as a strong acid and it has a high degree of ionisation in aqueous solution. It reacts with metals such as *Mg* and *Zn* to produce metal iodides and hydrogen gas.

$$Mg+2HI \rightarrow MgI_2+H_2$$

It reacts with metallic oxides, hydroxides and carbonates to form iodides.

$$ZnO+2HI \rightarrow ZnI_2+H_2O$$
$$NaOH+HI \rightarrow NaI+H_2O$$
$$Na_2CO_3+2HI \rightarrow 2NaI+H_2O+CO_2\uparrow$$

(b) *Stability and reducing properties* :

Hydrogen iodide is an unstable compound because its formation is accompanied by absorption of only 6·2 Kcal/mole.

$$H_2+I_2 \rightarrow 2HI\ (g)-12{\cdot}4\ \text{Kcal}$$

On heating to 180°, it undergoes dissociation to give hydrogen and iodine.

$$2HI \rightarrow H_2+I_2$$

It is the least stable hydrogen halide and is readily oxidised. Hence it acts as a strong *reducing agent*.

(i) *Reaction with Potassium Permangante solution* :

It reduces acidified $KMnO_4$ solution to Mn^{++} ion.

$$2KMnO_4+3H_2SO_4 \rightarrow K_2SO_4+2MnSO_4+3H_2O+5\ \text{'}O\text{'}$$
$$\underline{2HI+\text{'}O\text{'} \rightarrow H_2O+I_2\ [\times 5]}$$
$$2KMnO_4+3H_2SO_4+10HI \rightarrow K_2SO_4+2MnSO_4+8H_2O+5I_2$$

$(2MnO_4^-+16H^++10I^- \rightarrow 2Mn^{+2}+8H_2O+5I_2)$

(ii) *Reaction with Potassium Dichromate solution* :

It reduces acidified $K_2Cr_2O_7$ solution to Cr^{+3} ion.

$$K_2Cr_2O_7+4H_2SO_4 \rightarrow K_2SO_4+Cr_2(SO_4)_3+4H_2O+3\ \text{'}O\text{'}$$
$$\underline{2HI+\text{'}O\text{'} \rightarrow H_2O+I_2}$$
$$K_2Cr_2O_7+4H_2SO_4+6HI \rightarrow K_2SO_4+Cr_2(SO_4)_3+7H_2O+3I_2$$

(iii) *Reaction with MnO_2* : It reduces acidified MnO_2 to Mn^{++} ion.

$$\begin{array}{l} MnO_2+H_2SO_4\rightarrow MnSO_4+H_2O+\text{'O'} \\ 2HI+\text{'O'}\rightarrow H_2O+I_2 \\ \hline MnO_2+H_2SO_4+2HI\rightarrow MnSO_4+2H_2O+I_2 \end{array}$$

$$(MnO_2+4H^++2I^-\rightarrow Mn^{+2}+2H_2O+I_2)$$

(iv) *Reaction with H_2SO_4* : It reduces H_2SO_4 to SO_2.

$$H_2SO_4+2HI\rightarrow 2H_2O+SO_2+I_2$$

$$(SO_4^{-2}+4H^++2I^-\rightarrow 2H_2O+SO_2+I_2)$$

(v) *Reaction with HNO_3* : It reduces HNO_3 to NO_2.

$$2HNO_3+2HI\rightarrow 2H_2O+2NO_2+I_2$$

(vi) *Reaction with Ferric chloride* : It reduces $FeCl_3$ to $FeCl_2$.

$$2FeCl_3+2HI\rightarrow 2FeCl_2+2HCl+I_2$$

(vii) *Reaction with HNO_2* : It reduces to HNO_2 to NO.

$$\begin{array}{l} 2HNO_2\rightarrow H_2O+2NO+\text{'O'} \\ 2HI+\text{'O'}\rightarrow H_2O+I_2 \\ \hline 2HNO_2+2HI\rightarrow 2NO+I_2+2H_2O \end{array}$$

(viii) *Reaction with HIO_3* : It reduces HIO_3 to I_2.

$$HIO_3+5HI\rightarrow 3I_2+3H_2O$$

(ix) *Reaction with $CuSO_4$ solution.* : It reduces Cu^{+2} ion to Cu^+ (ous) ion.

$$\begin{array}{l} 2CuSO_4+2HI\rightarrow CuI_2+H_2SO_4\ [\times 2] \\ CuI_2\rightarrow Cu_2I_2+I_2 \\ \hline 2CuSO_4+4HI\rightarrow \underset{\text{cuprous iodide}}{Cu_2I_2}+I_2+2H_2SO_4 \end{array}$$

An aqueous solution of hydroiodic acid turns yellow on standing due to its oxidation to iodine by atmospheric oxygen.

$$4HI+O_2\rightarrow 2H_2O+2I_2$$

(c) *Reaction with Silver Nitrate* : It reacts with $AgNO_3$ solution to form yellow precipitate of silver iodide.

$$HI+AgNO_3\rightarrow AgI\downarrow+HNO_3$$

(d) *Reaction with Lead Acetate* : It reacts with lead acetate solution to give a yellow precipitate of lead iodide.

$$\underset{\text{Lead acetate}}{(CH_3COO)_2Pb}+2HI\rightarrow PbI_2\downarrow+2CH_3COOH$$

(e) *Reaction with Halogens* : Being more electronegative, all the other halogens replace iodine from hydriodic acid.

$$2HI+F_2\rightarrow 2HF+I_2$$

$$2HI+Cl_2\rightarrow 2HCl+I_2$$

$$2HI+Br_2\rightarrow 2HBr+I_2$$

(f) *Reaction with Mercuric chloride* : A red precipitate of mercuric iodide first formed dissolves in excess of the reagent to form a complex.

$$2HI+HgCl_2\rightarrow HgI_2\downarrow+2HCl$$

$$HgI_2+2HI\rightarrow \underset{\text{Complex}}{H_2[HgI_4]}$$

Uses : It is used :

(a) as a reducing agent in organic reactions,

(b) in the preparation of certain compounds of Iodine.

10.8. Comparision of Halogen Acids

Preparation and Properties	*HCl*	*HBr*	*HI*
Preparation→	By heating sodium chloride with conc. H_2SO_4 $NaCl+H_2SO_4 \rightarrow NaHSO_4+HCl$	By the action of bromine on the mixture of red phosphorus and water $2P+3Br_2 \rightarrow 2PBr_3$ $PBr_3+3H_2O \rightarrow H_3PO_3+3HBr$ $2P+5Br_2 \rightarrow 2PBr_5$ $PBr_5+4H_2O \rightarrow H_3PO_4+5HBr$	By the action of water on a mixture of iodine and red phosphorus $2P+3I_2 \rightarrow 2PI_3$ $PI_3+3H_2O \rightarrow H_3PO_3+3HI$
Properties :			
1. Physical state	Colourless gas	Colourless gas	Colourless gas
2. Smell	Pungent smelling gas	Pungent smelling gas	Pungent smelling gas
3. Solubility in water	Highly soluble	Highly soluble	Highly soluble
4. Stability	Stable	Less stable	Least stable
5. Action with ammonia	Gives white fumes of NH_4Cl $NH_3+HCl \rightarrow NH_4Cl$	Gives white fumes of NH_4Br $NH_3+HBr \rightarrow NH_4Br$	Gives white fumes of NH_4I $NH_3+HI \rightarrow NH_4I$

Preparation and Properties	HCl	HBr	HI
6. Acidic property	Acts as a strong acid and forms salts with alkalies and decomposes Na_2CO_3 $NaOH+HCl \rightarrow NaCl+H_2O$ $Na_2CO_3+2HCl \rightarrow 2NaCl+CO_2+H_2O$	Acts as a strong acid like HCl and forms salts with alkalies and deeomposes Na_2CO_3 $NaOH+HBr \rightarrow NaBr+H_2O$ $Na_2CO_3+2HBr \rightarrow NaBr+H_2O+CO_2$	Acts as an acid and forms salts with alkalies and decomposes Na_2CO_3 $NaOH+HI \rightarrow NaI+H_2O$ $Na_2CO_3+2HI \rightarrow 2NaI+H_2O+CO_2$
7. Reducing property	Acts as a reducing agent $MnO_2+4HCl \rightarrow MnCl_2+Cl_2+2H_2O$	Acts as a strong reducing agent $MnO_2+4HBr \rightarrow MnBr_2+Br_2+2H_2O$	Acts as a very strong reducing agent $2FeCl_3+2HI \rightarrow 2FeCl_2+2HCl+I_2$
8. Action with chlorine	It does not react	Bromine is liberated $Cl_2+2HBr \rightarrow 2HCl+Br_2$	Iodine is liberated $Cl_2+2HI \rightarrow 2HCl+I_2$
9. Action with H_2SO_4	It does not liberate chlorine	It liberates bromine $H_2SO_4+2HBr \rightarrow Br_2+SO_2+2H_2O$	It liberates iodine $H_2SO_4+2HI \rightarrow I_2+SO_2+2H_2O$
10. Action with $AgNO_3$ solution	Forms white ppt. which is soluble in NH_4OH $AgNO_3+HCl \rightarrow AgCl+HNO_3$ $AgCl+2NH_4OH \rightarrow [Ag(NH_3)_2]Cl+2H_2O$	Forms light yellow ppt. which is soluble in NH_4OH $AgNO_3+HBr \rightarrow AgBr+HNO_3$ $AgBr+2NH_4OH \rightarrow [Ag(NH_3)_2]Br+2H_2O$	Forms deep yellow ppt. which is insoluble in NH_4OH $AgNO_3+HI \rightarrow AgI+HNO_3$

10.9. Distinction Between Chlorides, Bromides and Iodides

Test	*Chlorides*	*Bromides*	*Iodides*
1. Compounds + MnO_2 + Conc. H_2SO_4 heat	Greenish yellow gas which turns moist starch iodide paper blue and bleached (A)	Reddish brown vapours of Br_2 which turns moist starch paper yellow (B)	Violet vapours of I_2 which turns moist starch paper blue (C)
2. Solution of compound + $AgNO_3$ solution	White ppt. of $AgCl$ soluble in NH_4OH and insoluble in HNO_3 (D)	Pale yellow ppt. of $AgBr$ sparingly soluble in NH_4OH and insoluble in HNO_3 (E)	Deep yellow ppt. of AgI, insoluble in NH_4OH and HNO_3 (F)
3. Confirmatory test	Chromyl chloride test—when heated with conc. H_2SO_4 and solid $K_2Cr_2O_7$, red vapours of CrO_2Cl_2 are produced. The latter on passing through water gives a yellow solution which on treatment with Lead acetate solution gives a yellow ppt. soluble in $NaOH$ (G)	CS_2 test—when shaken with a little Cl_2 water and CS_2, a brown CS_2 layer is obtained (H)	CS_2 test—when shaken with a little Cl_2 water and CS_2, a violet CS_2 layer is obtained (I)

A : $2NaCl+MnO_2+3H_2SO_4=2NaHSO_4+MnSO_4+2H_2O+Cl_2$
Cl_2
$2KI+Cl_2=2KCl+I_2$; Starch $+I_2\rightarrow$ Blue $\longrightarrow$ Bleached

B : $2NaBr+MnO_2+3H_2SO_4=2NaHSO_4+MnSO_4+2H_2O+Br_2$
Starch $+Br_2\longrightarrow$ yellow

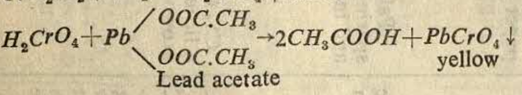
C : $2NaI+MnO_2+3H_2SO_4=2NaHSO_4+MnSO_4+2H_2O+I_2$
Starch $+I_2\longrightarrow$ Blue

D : $NaCl+AgNO_3=\underset{\text{white}}{AgCl\downarrow}+NaNO_3$
$AgCl+2NH_4OH=[Ag(NH_3)_2]Cl+2H_2O$
$AgCl+HNO_3\longrightarrow\times$

E : $NaBr+AgNO_3=\underset{\text{yellow}}{AgBr\downarrow}+NaNO_3$
$AgBr+2NH_4OH=[Ag(NH_3)_2]Br+2H_2O$
$AgBr+HNO_3\longrightarrow\times$

F : $NaI+AgNO_3=\underset{\text{yellow}}{AgI\downarrow}+NaNO_3$
$AgI+NH_4OH\longrightarrow\times$
$AgI+HNO_3\longrightarrow\times$

G : $NaCl+K_2Cr_2O_7+H_2SO_4\rightarrow CrO_2Cl_2+Na_2SO_4+K_2SO_4+H_2O$
$CrO_2Cl_2+2H_2O\rightarrow H_2CrO_4+2HCl$



$$H_2CrO_4+\underset{\text{Lead acetate}}{Pb\begin{matrix}/OOC.CH_3\\ \backslash OOC.CH_3\end{matrix}}\rightarrow 2CH_3COOH+\underset{\text{yellow}}{PbCrO_4\downarrow}$$

H : $2NaBr+Cl_2=2NaCl+Br_2$
$CS_2+Br_2\rightarrow$ Brown

I : $2NaI+Cl_2=2NaCl+I_2$
$CS_2+I_2\rightarrow$ Violet.

TYPICAL QUESTIONS

1. How iodine can act as both oxidising and reducing agent ? Give two examples for each.

Solution. Iodine as an oxidising agent :

(i) $H_2S+\underbrace{\underset{\text{O.A.}}{I_2^0}\xrightarrow{\qquad\qquad}2HI^{-1}}_{\text{Reduced (0 to }-1)}+S$

(ii) $\underbrace{\underset{\text{O A.}}{I_2^0}+2Na_2S_2O_3\rightarrow Na_2S_4O_6+2NaI^{-1}}_{\text{Reduced (0 to }-1)}$

Iodine as a reducing agent :

(i) $\underbrace{\underset{\text{R.A.}}{I_2^0}+5Cl_2+6H_2O\rightarrow 2HI^{+5}}_{\text{Oxidised (0 to 5)}}O_3+10HCl$

(ii) $\underbrace{\underset{\text{R.A.}}{I_2^0}+2KClO_3\rightarrow 2KI^{+5}}_{\text{Oxidised}}O_3+Cl_2$

2. $HBrO_4$ does not exist, why ?

Ans. The stability of HXO_4 arises due to π-bonding in XO_4^{-1}. In case of $HClO_4$, there is π-bonding between $3d$ of chlorine and $2p$ of oxygen. The extension of $4d$ is more in space and hence there is no effective π-bonding between $4d$ and $2p$. Due to this $HBrO_4$ does not exist.

3. Why HI is not prepared by the action of conc. H_2SO_4 on NaI ?

Ans. When NaI reacts with conc. H_2SO_4 HI is obtained. Hydrogen iodide (HI) is a reducing agent and conc. H_2SO_4 is an oxidising agent. Hence both reacts to give Iodine, SO_2 etc.

$$2NaI + H_2SO_4 \xrightarrow{\text{heat}} Na_2SO_4 + 2HI$$
$$\underset{\text{R.A.}}{2HI} + \underset{\text{O.A.}}{H_2SO_4} \longrightarrow 2H_2O + I_2 + SO_2$$
$$\overline{2NaI + 2H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O + I_2 + SO_2}$$

4. Compound A is heated with conc. H_2SO_4 to give a gas B. The gas B reacts with $NaOH$ to give a salt C which gives white precipitate 'D' with $AgNO_3$ solution. The precipitate 'D' reacts with NH_4OH to give solution 'E' and the solution 'E' gives white precipitate, F ith HNO_3. A gives golden yellow flame. Identify A, B, C, D, E and F and write down the reaction.

Ans.

$$\begin{tikzcd}
A \arrow[r, "\text{Conc. } H_2SO_4", "\text{heat}"'] \arrow[d] & B \text{ (gas)} \arrow[r, "NaOH"] & C \text{ (salt soln.)} \arrow[r, "AgNO_3"] & D \text{ (white ppt.)} \arrow[r, "NH_4OH"] & E \text{ (soln.)} \arrow[d, "HNO_3"] \\
\text{Golden yellow flame} & & & & F \text{ (white ppt.)}
\end{tikzcd}$$

White precipitate with $AgNO_3$ solution, means that it is chloride.
$A = NaCl$; $B = HCl$; $C = NaCl$; $D = AgCl$; $E = [Ag(NH_3)_2]Cl$; $F = AgCl$.

$$\underset{(A)}{NaCl} + H_2SO_4 \xrightarrow{\text{heat}} NaHSO_4 + \underset{(B)}{HCl}.$$

$$\underset{(B)}{HCl} + NaOH \longrightarrow \underset{(C)}{NaCl} + H_2O$$

$$\underset{(C)}{NaCl} + AgNO_3 \rightarrow \underset{(D)}{AgCl\downarrow} + NaNO_3$$

$$\underset{(D)}{AgCl} + 2NH_4OH \rightarrow \underset{(E)}{[Ag(NH_3)_2]Cl} + 2H_2O$$

$$\underset{(E)}{[Ag(NH_3)_2Cl} + 2HNO_3 \rightarrow \underset{(F)}{AgCl} + 2NH_4NO_3.$$

5. At S.T.P. HF is a liquid but HCl is a gas. Explain.

Ans. HF forms associated molecule due to hydrogen bond. Hence its melting point becomes high. Since chlorine atom is big, hence HCl does not form hydrogen bond. Therefore, its melting point is low. Hence HF is a liquid but HCl is a gas.

6. Chlorine has higher electron-affinity than fluorine. Explain.

Ans. See Periodic Table.

QUESTION

LONG TYPE QUESTION

1. Justify the position of Fluorine, Chlorine, Bromine and Iodine in the Periodic table.
2. Describe the preparation of pure and dry chlorine with a neat sketch. [R. U. 1967 A; Bhag. U. '66 S] Explain with equations the action of chlorine on
   (i) Slaked lime,
   (ii) Quick lime,
   (iii) Sulphur dioxide, [M. U. 1977 A]
   (iv) Potassium iodide,
   (v) Caustic Soda, **[M. U. 1969 S; R. U. '68 S]**
   (vi) Sulphurous acid,
   (vii) Ammonia. **[M. U. 1969 S; R. U. '68 S]**
3. How fluorine is prepared in the laboratory ? Describe its chemical behaviour.
4. Decribe with a neat diagram, the laboratory method of preparation of hydrogen chloride. Answer the following questions giving reasons for your answer.
   (a) Can a similar method be applied in the preparation of HBr ?
   (b) Can you prepare a highly concentrated solution of hydrochloric acid by the distillation of a dilute solution ?
   What is the composition of aqua regia ?
   [P. U. 1975 A; B. U. '73 S; R. U. '74 A]
5. What are the usual sources of bromine in nature ? How is bromine prepared (a) in the laboratory, (b) industrially ?
   [R. U. 1973 A; M. U. '73 A; Mith. U. '75 A]
   Mention the important uses of bromine. You are given a sample of brown gas. What can it be ? How would you proceed to identify it ?
   [P. U. 1973 A; Bhag. U. '73 S]
6. Describe with the sketch of the apparatus, the preparation of hydrobromic acid gas in the laboratory.
   How is an aqueous solution of the acid prepared ?
   Why this gas is not prepared in a similar manner used in the preparation of hydrochloric acid gas ? What happens when the acid (a) is exposed to sunlight in the presence of air and (b) acts on (i) metallic magnesium, (ii) MnO_2 ?
   [P. U. 1973 A; B. U. '65 A; M. U. '74 A; Mith. U. '75 A]
7. Describe with a neat sketch of the apparatus, the laboratory method for preparation of hydrogen iodide and an aqueous solution of hydroiodic acid. Why is it not prepared in the same way as hydrochloric acid ? **[R. U. 1976 A]**
8. The given salt may be chloride, bromide and iodide. How would you identify it ? **[B. U. 1966 A; R. U. '73 A, '74 S; Bhag. U. '76 A; P. U. '78 A]**
9. How does bromine occur in nature ? How is it isolated in pure state ? How does it react with H_2S, SO_2 and $NaOH$? **[BIEC 1984]**
10. How would you prepare iodine from caliche ? How does iodine react with :
    (a) Conc. HNO_3 (b) $KClO_3$ (c) Cold and dil. $NaOH$ solution (d) H_2S ?
    Give equation. **[M. U. 1981 A]**

11. What are the principles involved in the manufacture of Iodine from sea weeds ? How does it react with (a) caustic soda (b) potassium chlorate (c) conc. HNO_3 ? Write its important uses. **[BIEC 1985]**

12. Outline the chief points of similarity and dissimilarity of the halogens.

13. (a) How is chlorine obtained on a large scale ?

(b) Explain with the help of equations the reaction of chlorine on the following :

(i) water (ii) carbon monoxide (iii) cold solution of sodium hydroxide iv) a solution of potassium iodide (v) powered antimony (vi) stannous chloride.

14. Describe laboratory method for the preparation of chlorine.

How is it freed from hydrochloric acid and moisture ? Explain the action of chlorine on (a) slaked lime (b) hydrogen sulphide solution (c) hydrogen bromide solution (d) carbon monoxide.

[R. U. 1978; M. U. '69; Mith. U. '80; Bhag. U. '69]

15. (a) (i) Draw a labelled diagram of an electrolytic cell used for the manufacture of chlorine from common salt solution.

(ii) What is the action of chlorine on caustic soda at room temperature ? Give equation.

(b) (i) How is bromine manufactured from sea water ? Give equation of the reaction.

(ii) Mention two industrial uses of bromine.

16. (a) Describe, giving a neat and labelled diagram the manufacture of bromine. **[P. U. 1970 A]**

(b) How does it react with

(i) NH_3 (ii) Sodium sulphite solution (iii) hot caustic soda solution (iv) KI ? **[P. U. 1970 A]**

(c) What is the action of conc. hydrochloric acid on

(i) Manganese dioxide (ii) Potassium Permanganate (iii) Sodium thiosulphate (iv) H_2O_2 ?

17. Describe the manufacture of bromine from carnallite and state its uses. How does it react with (a) KI solution (b) hot $NaOH$ solution (c) SO_2 solution (d) Phosphorus ?

18. (a) How is pure iodine obtained from seaweeds ? **[P. U. 1973 A; Mith. U. '75 A; M. U. '76 A; Bhag. U. '74 A; R. U. '73 A, '75 A]**

(b) Explain, giving equations, what happens when iodine reacts with :

(i) Sodium thiosulphate (ii) Potassium nitrite (iii) Sulphur dioxide solution

(iv) solution of KI (v) HNO_3 **[P. U. 1973 A; Mith. U. '73 A]**

(vi) Caustic potash. **[P. U. 1973 A; Mith. U. '73 A]**

(c) What is the action of conc. HCl on

(i) MnO_2 (ii) Pb_3O_4 (iii) $K_2Cr_2O_7$ (iv) H_2O_2 ?

19. (a) What are the sources of iodine ?

(b) Describe any one process for the manufacture of Iodine.

(c) State with equations and conditions the reactions of iodine with

(i) red phosphorus [P. U. 1973 A] (ii) nitric acid (iii) cold and dilute alkali (iv) $Na_2S_2O_3$ (v) dry HgO (vi) moist Ag_2O and (vii) Iron filings.

[P. U. 1974 A]

SHORT ANSWER TYPE QUESTIONS

20. Which elements are known as halogens ? Why are these elements known as halogens ?

Hint : F, Cl, Br, I, Halogen Greek words hals and genas meaning sea salts producer. Since the salts of these elements are present in sea water, they are so named.

21. What happens when bromine gas is passed in aqueous solution of SO_2 ?

22. Compare the bleaching property of Cl_2 and SO_2.

Hint : See SO_2 and Cl_2 both.

23. Give the equations for the reactions of chlorides and bromides with concentrated H_2SO_4.

24. Account the following (or Explain the following or Give reasons for the following) :

(i) HCl is prepared by the action of conc. H_2SO_4 on $NaCl$.

(ii) HI unlike HCl cannot be prepared by the action of conc. H_2SO_4 on NaI.

(iii) I_2 is soluble in KI.

(iv) I_2 is an oxidising and reducing agent both.

(v) HI is stronger than HBr.

(vi) Cl_2 can displace bromine from bromide but not F_2 from fluoride.

(vii) HBr is not prepared by the action of conc. H_2SO_4 on a bromide.

[BIEC 1985]

Hint : (i) HCl is more volatile than H_2SO_4 (ii) see typical question (iii) complex formation KI_3 (iv) see typical question (v) see acid base (vi) since Cl_2 is more electronegative than bromine but less than F_2.

25. Arrange the following according to the instruction given in the bracket :

(i) $HOCl$, HOI, $HOBr$ (increasing acidic strength)
(ii) HCl, HI, HBr (increasing acidic strength)
(iii) Cl_2, I_2, Br_2 (increasing bleaching property)
(iv) $HOCl$, $HClO_2$, $HClO_3$, $HClO_4$ (increasing acidic strength)
(v) I_2, Cl_2, F_2, Br_2 (increasing acidic nature)
(vi) Cl_2, F_2, Br_2, I_2 (increasing E.A.)
(vii) I_2, Cl_2, Br_2, F_2 (increasing I.P.)
(viii) I_2, F_2, Br_2, Cl_2 (increasing solubility in water)
(ix) F_2, I_2, Br_2, Cl_2 (increasing reactivity)
(x) F_2, I_2, Cl_2, Br_2 (increasing metallic nature)
(xi) F_2, I_2, Cl_2, Br_2 (increasing acidic nature)
(xii) F_2, I_2, Cl_2, Br_2 (increasing M.P., density)
(xiii) F_2, Cl_2, I_2, Br_2 (increasing solid nature)
(xiv) F_2, I_2, Cl_2, Br_2 (increasing reducing property)
(xv) I_2, Cl_2, Br_2, F_2 (increasing atomic size).

[**Hint** : Take the help of periodic discussion summary]

26. Fill up the blank and balance :

(1) $KNO_2+KI+HCl \rightarrow ....+KCl+H_2O+NO.$ [I.I.T. 1969]
(2) $P+Br_2+H_2O \rightarrow ....+H_3PO_3.$ [I.I.T. 1969]
(3) $I_2+Na_2S_2O_3 \rightarrow Na_2S_4O_6+.........$ [I.I.T. 1969]
(4) $NaBr+MnO_2+H_2SO_4 \rightarrow NaHSO_4+.........+.........+H_2O.$ [I.I.T. 1969]

(5) I_2+HNO_3(conc.) $\xrightarrow{\text{heat}}$ ....+.......+.......... [I.I.T. 1979]

(6) $Cl_2+Ca(OH)_2 \xrightarrow{\text{hot}}$ ....+.........+......... [I.I.T. 1970]

(7) $Ca(OCl)Cl+NaI+HCl \rightarrow CaCl_2+H_2O+NaCl+$......... [I.I.T. 1970]

(8) $Mn_3O_4+HCl \rightarrow MnCl_2+H_2O+$......... [I.I.T. 1971]

(9) $NH_3+NaOCl \rightarrow N_2+NaCl+$......... [I.I.T. 1971]

(10) $HI+H_2SO_4 \rightarrow$.........+.........+......... [I.I.T. 1971, '72]

(11) $CuSO_4+KI \rightarrow$.........+.........+.........

(12) $Br_2+OH^- \rightarrow BrO^{-1}+$.........$+H_2O$. [I.I.T. 1974]

(13) $K_2Cr_2O_7+HCl \rightarrow 2KCl+CrCl_3+H_2O+$......... [I.I.T. 1975[

(14) $KMnO_4+KCl+H_2SO_4 \rightarrow K_2SO_4+MnSO_4+H_2O+$......... [I.I.T. 1976]

(15) NH_3+Cl_2(excess)$\rightarrow$.........+......... [I.I.T. 1976]

(16) $Cl_2+OH^- \rightarrow$.........$+ClO_3^{-1}+$......... [I.I.T. 1977]

(17) $MnO_2+HCl \rightarrow MnCl_2+H_2O+Cl_2$ [I.I.T. 1977; BIT '83]

(18) $HNO_3+HI \rightarrow NO+I_2+H_2O$. [I.I.T. 1978]

(19) $Cl_2+IO_3^{-1}+OH^- \rightarrow IO_4^{-1}+Cl^-+H_2O$. [I.I.T. 1978]

(20) $AgCl+NH_4OH \rightarrow$.........+.........

(21) I_2+Cl_2+.........$\rightarrow HIO_3+$.........

(22) $HCl+KMnO_4 \rightarrow KCl+MnCl_2+$.........+.........

(23) SO_2+Cl_2+.........$\rightarrow H_2SO_4+$..........

(24) $I_2+KI \rightarrow$..........

27. Fill up the blank :

(A) (i) When Cl_2 is passed into cold and dil. KOH solution then———and———are obtained. (ii) $NaCl$ with conc. H_2SO_4 on heating gives a gas———. (iii) I_2 reacts with hot and conc. $NaOH$ solution to give NaI and———. [I.I.T. 1980]

(B) (i) 2 moles of $KMnO_4$ react with excess of HCl to give——— of Cl_2 in cold condition. (ii) In the manufacture of Cl_2 by Down process———is used, (iii) The colour of iodine is decolourised by———. (iv) Cl_2 bleaches moisture flower due to———and bleaching is———.

28. Match type :

Match *A* with *B*.

A	*B*
(1) Cl_2	(a) Strong reducing agent
(2) Br_2	(b) Hydrogen bond
(3) I_2	(c) Bleaching agent
(4) HF	(d) Liquid
(5) HI	(e) Sublime.

29. Mixed Type :

(i) A gas X reacts with sodium to give salt Y. Y gives white precipitate with $AgNO_3$. The precipitate is soluble in NH_4OH but insoluble in HNO_3. Identify X, Y and Z.

(ii) When a salt A is heated with conc. H_2SO_4 then colourless gas B is obtained. B gives white precipitate C with $AgNO_3$ solution. B gives greenish yellow gas D with MnO_2. The original salt gives golden yellow colour in flame test. Identify A, B, C, D.

Select and write the Correct answer from the following.

30. Which of the following has got highest electron-affinity ?
(1) F (2) Cl (3) Br (4) I (5) H. [MDAT 1983]

31. Which of the gases are obtained when mixture of $NaCl$ and NaI is heated with conc. H_2SO_4 ?
(1) HCl, HI (2) HCl, I_2 (3) HCl, I_2, SO_2 (4) HCl, HI, Na_2SO_4
(5) None of these.

32. Which of the following has got biggest atomic size ?
(1) F (2) Cl (3) I (4) Br. [CEET 1980]

33. Which of the following is the strongest reducing agent ?
(1) HCl (2) HI (3) HBr (4) HF. [CEET 1980]

34. Which of the following has got highest I.P. ?
(1) Cl_2 (2) F_2 (3) Br_2 (4) I_2. [BIEC 1980]

35. Which of the following halogen can displace two halogens from solution of the salt ?
(1) Cl_2 (2) F_2 (3) Br_2 (4) I_2.

36. Chlorine bleaches a substance due to :
(1) oxidation (2) reduction (3) addition (4) displacement.

37. Which of the following turns moist starch paper blue ?
(1) Cl_2 (2) I^- (3) Cl^- (4) I_2 (5) more than one.

38. On boiling an aqueous solution of $KClO_3$ with iodine the following product is obtained.
(1) KIO_4 (2) KIO_3 (3) KCl (4) K_2O. [NCERT 1980]

39. In the preparation of Cl_2 from HCl, MnO_2 acts as
(1) Reducing agent (2) Oxidising agent
(3) Catalytic agent (4) Dehydrating agent. [CPMT 1981]

40. Colour of iodine solution is discharged by shaking it with an aqueous solution of :
(1) H_2SO_4 (2) Na_2S (3) $Na_2S_2O_3$ (4) Na_2SO_4. [CPMT 1981]

41. The reaction of sodium thiosulphate with iodine gives :
(1) Sodium tetrathionate (2) Sodium sulphite
(3) Sodium sulphide (4) Sodium sulphate. [CPMT 1981]

42. Of the following species the one which is non-existent is :
(1) XeF_5 (2) BrF_5 (3) SbF_5 (4) PF_5. [NCERT 1980]

43. It has been observed that gaseous HCl is a very poor conductor of electricity. But a solution of HCl in water is a good conductor. This is due to the reason that : [NCERT 1976]
(1) Water is a good conductor of electricity.
(2) HCl in water solution ionises.
(3) A gas cannot conduct electricity but a liquid can.
(4) HCl gas does not obey Ohm's law whereas the solution does.

44. Bromine is manufactured from :
(1) sea water (2) Deacon's process (3) electrolysis of sodium bromide
(4) carnallite. [CEET 1976]

□□□

CHAPTER 11

METALS AND GENERAL METALLURGICAL OPERATIONS

11.1. Metals and non-metals

The elements are classified into two main groups—metals and non-metals. There are certain characteristic properties by means of which we can distinguish between metals and non-metals. It may, however, be noticed that there is no sharp line of division between metals and non-metals. Some important characteristics of metals and their distinction from non-metals are described below :

S. No.	*Property*	*Metals*	*Non-metals*
1.	**Physical state**	Metals are solids at ordinary temperatures. (*Exception* : Mercury is a liquid)	Non-metals exist in all the three states.
2.	**Melting and Boiling points**	They have high melting and boiling points. (*Exception* : Alkali metals)	They have low melting and boiling points. (*Exceptions* : Boron, Carbon, Silicon)
3.	**Density and hardness**	They have a high specific gravity and are generally hard. (*Exceptions* : *Li*, *Na*, *K*)	They have a low specific gravity and are generally not hard. (*Exception*: Diamond is the hardest substance known.)
4.	**Malleability and ductility**	They are malleable and ductile. Hence, they can be beaten into sheets of fine thickness and drawn into wires. (*Exceptions* : *As*, *Sb* and *Bi*)	They are not malleable and ductile. On the other hand, they are brittle. Hence, they cannot be beaten into sheets or drawn into wires.
5.	**Conductivity**	They are good conductor of heat and electricity. (*Exception* : Lead)	They are poor conductors of heat and electricity. (*Exceptions* : Graphite and Gas Carbon)

S. No.	*Property*	*Metals*	*Non-metals*
6.	**Metallic lustre**	They possess a shining lustre, known as metallic lustre, particularly on a freshly polished surface.	They do not possess a metallic lustre. (*Exceptions* : Iodine and Graphite)
7.	**Ionisation Energy**	They have low ionisation energies (less than 220 kcal./mole).	They have high ionisation energies (greater than 220 kcal./mole)
8.	**Electro-negativity and electro-chemical nature**	They have low values of electronegativity, generally 1·7 and less. They form cations in solution and are obtained at the cathode during electrolysis. They are, therefore, electropositive in nature.	They have high values of electronegativity, generally 2·1 and more. They form anions in solution and are obtained at the anode during electrolysis. They are, therefore, electro-negative in nature. (*Exception* : Hydrogen)
9.	**Type of Bonds**	Their atoms are linked by metallic bonds.	Their atoms are generally linked by covalent bonds.
	CHEMICAL :		
10.	**Nature of Oxides**	They form basic oxides. *Exception* : CrO_3 Mn_2O_7 are acidic; Al, Sn, Zn oxides are amphoteric.	They form acidic oxides. *Exception* : CO, NO, N_2, H_2O are neutral.
11.	**Formation of Hydrides**	Only a few metals form hydrides (NaH, CaH_2 etc.) with hydrogen. These are unstable compounds.	They form stable hydrides with hydrogen.
12.	**Oxidising or reducing agents**	They act as reducing agents since their atoms readily donate electrons. $Na \rightarrow Na^+ + e$	They act as oxidising agents since their atoms readily accept electrons. $Cl + e \rightarrow Cl^{-1}$
13.	**Action of acids**	They dissolve in mineral acids with the formation of a salt and evolution of a gas. $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$ $Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$	They either do not dissolve in mineral acids or they form oxy-acids. $S + 6HNO_3 \rightarrow H_2SO_4 + 6NO_2 + 2H_2O$ $P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

11.2. Occurrence of metals : Very few metals e.g. copper, silver, gold, platinum occur in nature in the free or natural state. Usually metals are found in the combined state in the earth's crust. The natural occurring inorganic substances are known as *minerals*. Minerals are not economical for the extraction of metals. Those minerals from which the metal can be extracted economically are called ores. Thus all ores are minerals but all minerals are not ores. For example—cinnabar (HgS) is an ore as well as mineral of mercury but iron pyrite (FeS_2) is a mineral of iron, not the ore because iron in not extracted from iron pyrite. The chief ores in the order of economic importance are (1) oxides, (2) sulphides, (3) carbonates, (4) sulphates (5) halides and (6) silicates. Thus metals occur in nature as :

(a) **Free or native** : Silver, Gold, Platinum etc.

(b) **Oxides** : Metals, (Copper, Zinc, Iron, Aluminium.)

Example : (i) Cuprite (Cu_2O), (ii) Zincite (ZnO), (iii) Haematite (Fe_2O_3), (iv) Bauxite ($Al_2O_3\ 2H_2O$).

(c) **Sulpides** : (i) Copper pyrites, $CuFeS_2$; (ii) Galena, PbS; (iii) Cinnabar, HgS; (iv) Iron pyrite, FeS_2.

(d) **Carbonates** : (i) Malachite, $CuCO_3$, $Cu(OH)_2$; (ii) Calamine $ZnCO_3$; (iii) lime stone, $CaCO_3$; (iv) Siderite, $FeCO_3$.

(e) **Sulphates** : (i) Epsomite, $MgSO_4.\ 7H_2O$; (ii) Gypsum, $CaSO_4.\ 2H_2O$; (iii) Anglesite, $PbSO_4$; (iv) Anhydrite, $CaSO_4$.

(f) **Halides** : (i) Rock salt, $NaCl$; (ii) Horn silver, $AgCl$; (iii) Fluorspar, CaF_2; (iv) Carnallite, $KCl.\ MgCl_2,\ 6H_2O$.

(g) **Silicates** : (i) Asbestos, $CaMg_3(SiO_4)$; (ii) Mica, $KAl_3Si_3\,O_{10}(OH)_2$; (iii) Felspar, $KAl\,(Si_3O_8)$.

11.3. Metal and Their Important Minerals or Ores :

Metals	*Minerals/ores with their Chemical Formulae*
1. Sodium (IA, alkali metal)	(a) Rock Salt—$NaCl$; (b) Chile salt petre—$NaNO_3$; (c) Borax—$Na_2B_4O_7.10H_2O$.
2. Potassium (IA, alkali metal)	(a) Sylvine—KCl; (b) Carnallite—$KCl.MgCl_2.6H_2O$; (c) Felspar—$K_2O.Al_2O_3.6SiO_2$.
3. Copper (IB, coinage metal)	(a) Cuperite, Cu_2O; (b) Malachite, $CuCO_3.\ Cu(OH)_2$; (c) Copper glance, Cu_2S; (d) Copper pyrite, $CuS.FeS$; (e) Azurite, $2CuCO_3.Cu(OH)_2$.
4. Silver (IB, best conductive metal)	(a) Horn silver, $AgCl$; (b) Lunar caustic, $AgNO_3$; (c) Silver glance, Ag_2S; (d) Ruby silver, $3Ag_2S.Sb_2S_3$.

Metals	*Minerals/ores with their Chemical Formulae*
5. Calcium (IIA, alkaline earth metal)	(a) Limestone, Chalk, Marble, Iceland spar Calcite– $CaCO_3$; (b) Dolomite, $MgCO_3.CaCO_3$; (c) Gypsum, $CaSO_4.2H_2O$; (d) Anhydrite, $CaSO_4$; (e) Phosphorite, $Ca_3(PO_4)_2.Ca(OH)_2$; (f) Bone, $Ca_3(PO_4)_2$; (g) Fluorapatite, $3CaF_2.\ Ca_3(PO_4)_2$; (h) Chlorapatite, $3CaCl_2.Ca_3(PO_4)_2$.
6. Magnesium (IIA, bridge metal)	(a) Carnallite, $KCl.MgCl_2.6H_2O$; (b) Dolomite, $MgCO_3.CaCO_3$; (c) Magnesite, $MgCO_3$; (d) Epsomite, $MgSO_4.7H_2O$; (e) Kisserite, $MgSO_4.H_2O$.
7. Barium (IIA, alkaline earth metal)	(a) Heavy spar, $BaSO_4$; (b) Witherite, $BaCO_3$.
8. Zinc (IIB, amphoteric metal)	(a) Zinc blende, ZnS; (b) Zincite, ZnO; (c) Calamine, $ZnCO_3$; (d) Willemite, $ZnSiO_3$.
9. Mercury (IIB, liquid metal)	(a) Cinnabar, HgS.
10. Aluminium (IIIA, amphoteric metal)	(a) Bauxite, $Al_2O_3.2H_2O$; (b) Corundum, Al_2O_3; (c) Felspar, $KAlSi_3O_8$; (d) Clay Silicate , $Al_2O_3.\ 2SiO_2.\ 2H_2O$; (e) Cryolite, $3NaF.AlF_3$; (f) Alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$; (g) Mica; (h) Diaspore, $Al_2O_3.H_2O$; (i) Lapis Lazuli, Sodium aluminium silicate with sulphur (Blue in colour).
11. Tin (IVA, amphoteric metal)	(a) Cassiterite or Tin stone, SnO_2; (b) Stannite, $Cu_2S.\ FeS.SnS_2$.
12. Lead (IVA, amphoteric metal)	(a) Galena, PbS; (b) Cerussite, $PbCO_3$; (c) Anglessite, $PbSO_4$; (d) White Lead, $2Pb(OH)_2.PbCO_3$.
13. Chromium (VIB, transition metal)	(a) Chromite, $FeCr_2O_4$; (b) Chrome ochre, Cr_2O_3.
14. Manganese (VIIB, transition metal)	(a) Pyrolusite, MnO_2; (b) Mn-spar, $MnCO_3$; (c) Braunite, Mn_2O_3.
15. Iron (VIII, transition metal)	(a) Iron Pyrite, FeS_2; (b) Siderite, $FeCO_3$; (c) Red haematite, Fe_2O_3; (d) Magnetite, Fe_3O_4; (e) Limonite, $2Fe_2O_3,3H_2O$.

11.4. Terms used in Metallurgy

Calcination :

It is a process in which the ore is subjected to the action of heat but is confined to those operations only in which matter is simply expelled or the physical structure altered when heat is applied. Here presence of air is not essential nor it is necessary to exclude it.

For example, when limestone is heated, carbon dioxide is given off, and then it is said to be calcined. When bauxite is calcined at high temperatures water is removed and anhydrous alumina is left. Magnestite ($MgCO_3$) on calcination gives magnesia (MgO).

$$CaCO_3 \rightarrow CaO + CO_2\uparrow$$

$$\underset{\text{Bauxite}}{Al_2O_3.2H_2O} \rightarrow Al_2O_3 + 2H_2O$$

$$\underset{\text{Malachite}}{CuCO_3.Cu(OH)_2} \rightarrow 2CuO + H_2O + CO_2\uparrow$$

$$\underset{\text{Dolomite}}{CaCO_3.MgCO_3} \rightarrow CaO + MgO + 2CO_2\uparrow$$

$$\underset{\text{Magnesite}}{MgCO_3} \rightarrow MgO + CO_2\uparrow$$

Roasting :

It is the process in which the ore is heated above its melting point in presence of air so that volatile impurities are removed and chemical change takes place. It is a redox process.

Some of the oxidation reactions of sulphide ores are given below.

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$

$$HgS + O_2 \rightarrow Hg + SO_2$$

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

Calcination is also roasting but in this case, we are concerned with the changes due to the expulsion of some ingredient only, and no other chemical change.

Smelting :

The process of extracting a metal in the state of fusion is called smelting. In this process the ore is mixed with carbon after roasting and heated in a suitable furnace. A suitable flux is added during the operation to convert the non-fusible gangue to fusible slag. The metallic oxide is reduced by carbon and the metal may be obtained in the molten state or as vapours which are condensed. Metals like zinc, tin or lead, iron are obtained by this process.

$$ZnO + 2C \rightarrow Sn + 2CO\uparrow$$

$$SnO_2 + C \rightarrow Zn + CO\uparrow$$

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2\uparrow$$

Flux :

Flux is a substance that is added to the ore during smelting (a) to decrease the melting point, (b) to make the ore conducting and (c) to remove total impurities (basic and acidic). On this basis flux is of three types : (i) Neutral flux, (ii) Acidic flux and (iii) Basic flux.

(i) Neutral Flux : (a) The melting point of sodium chloride ($NaCl$) alone is 820°C but when it is mixed with KF or CaF_2 then its melting point is decreased to 600°C. (b) Similarly alumina (Al_2O_3) is bad conductor of electricity but when cryolite [$3NaF.AlF_3$] (flux) is added to it then it becomes good conductor and the melting point is decreased. Hence KF, CaF_2, cryolite etc. are known as neutral flux.

(ii) Acidic Flux : If the ore contains basic impurities such as CaO, FeO etc. then it is removed by acidic flux (SiO_2) by forming slag.

$$\underset{\text{Impurity}}{CaO} + \underset{\text{Flux (acid c)}}{SiO_2} \rightarrow \underset{\text{Slag}}{CaSiO_3}$$

$$FeO + SiO_2 \rightarrow FeSiO_3$$

(iii) Basic Flux : If the impurities in the ore are acidic (SiO_2) in nature, a basic flux CaO, MgO, FeO etc. are added. The impurities gangue or matrix present in the ore react with flux to form fusible slag which does not mix with the molten metal and forms the upper layer. It is removed.

$$\underset{\text{Flux}}{CaO} + \underset{\text{Impurity}}{SiO_2} \rightarrow \underset{\text{Slag}}{CaSiO_3}$$

Slag :

The slag is a substance which is formed by the combination of impurities and flux. These are fusible materials.

Impurities + Flux = Slag.

The slag is immiscible with the metal and has a low melting point and density. The slag floats on the metal and protects it from oxidation. It is removed from the furnace through the slag hole. Slags are usually silicates.

$$\underset{\text{Impurity}}{CaO} + \underset{\text{Flux}}{SiO_2} \rightarrow CaSiO_3 \text{ (slag)}$$

Gangue or Matrix :

The impurities present in the ore or mineral are known as gangue or matrix. The gangue or matrix present in the ore is refractory or non fusible in nature but it reacts with the flux forming fusible slag which does not mix with the molten metal and forms the upper layer.

11.5. Mineral Wealth of India

Metal	*Indian source*
(i) Gold	Auriferrous deposits of Kolar Gold Field in Karnataka and also alluvial sand.
(ii) Copper	Machite in Singhbhum, Hazaribagh (Bihar), Khetri (Rajasthan).
(iii) Iron	Orissa, Bihar, Madhya Pradesh, Mysore, Goa. Besides these states, other states are Uttar Pradesh, Tamil Nadu, Punjab, Rajasthan etc.
(iv) Aluminium	Bauxite and corundum are found in Rewa, Bhopal, Orissa, Bihar, Tamil Nadu etc.
(v) Tin	Bihar, Orissa and Rajasthan.
(vi) Lead	Bihar, Madhya Pradesh and Rajasthan.
(vii) Calcium	Limestone occurs in Satna, Katni, Rohtasgarh.

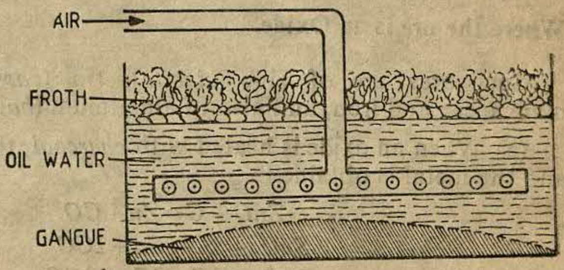
11.6. Metallurgy : *The extraction of a pure metal from its ore is called metallurgy.* Each metal presents an individual problem in metallurgy depending upon chemical properties and nature of the ore from which it is to be extracted. It involves three main steps :

(1) Concentration of the ore, (2) Extraction of the metal,
(3) Purification or refining of the metal.

11.7. Methods Employed in the Concentration of the Ores

(i) Levigation : Generally metal ores are heavier than the gangue associated with them. By flowing the powdered ore in a current of water the lighter rocky and earthy impurities can be washed away over much longer distances than the heavier ore particles. The ore particles are left behind.

(ii) Froth floatation method : This is one of the convenient methods used to concentrate sulphide ores. In this method, the finely powdered ore is mixed with water. One or more frothing agents are added. Then air is blown through the mixture. A



froth is formed. The ore particles rise to the surface, carried by the froth. The earthy impurities are wetted by water and sink to the bottom. The froth is skimmed off. Acid is added to break up the froth. The concentrated ore is filtered and dried.

(iii) **Leaching** : In this method the powdered ore is treated with a suitable dissolving agent. It dissolves the ore but not the impurities. Thus bauxite, an ore of aluminium, besides Al_2O_3 contains impurities like Fe_2O_3 SiO_2. The powdered bauxite is leached with a strong solution of sodium hydroxide. Al_2O_3 dissolves forming sodium aluminate. The impurities remain undissolved. These are filtered, dried and ignited. Al_2O_3 is obtained in a pure form.

$$Al_2O_3+6NaOH \rightarrow 2Na_3AlO_3+3H_2O$$
$$Na_3AlO_3+3H_2O \rightarrow 3NaOH+Al(OH)_3$$
$$2Al(OH)_3 \rightarrow Al_2O_3+3H_2O$$

Leaching is also employed to concentrate silver ores and to bring native gold into solution from rocks containing threads and particles of gold. In both cases, leaching is done using a dilute solution of sodium or potassium cyanide.

$$Ag_2S+4NaCN \rightarrow 2Na[Ag(CN)_2]+Na_2S$$
$$4Au+8KCN+2H_2O+O_2 \rightarrow 4K[Au(CN)_2]+4KOH$$

(iv) **Liquation** : This process is employed to concentrate ores having lower melting points than the impurities. Thus the ore of antimony stibnite, which has a low melting point, can be concentrated by heating the powdered ore on the sloping floor of a furnace. The temperature is adjusted to be just above the melting point of the ore. The ore melts and flows away. Infusible impurities are left behind.

11.8. General Principles of Metallurgy (Extraction of Metals)

The process of metallurgy would necessarily depend on nature of the ore of the substance which is to be worked out for the metal. In this section, we shall deal with a few broad methods generally used for the isolation of metals.

Where the ore is an Oxide.

Such ores are of zinc (*zincite*), tin (*cassiterite*), chromium, manganese and iron, and also of aluminium (*bauxite*).

(a) When an oxide is heated with *charcoal*, the oxide is reduced and the metal is obtained.

$$ZnO+C \rightarrow Zn+CO$$
$$SnO_2+2C \rightarrow Sn+2CO$$
$$Fe_2O_3+3C \rightarrow 2Fe+3CO$$

(b) Sometimes the oxide of a refractory metal is reduced by aluminium. In the *Goldschmidt thermit process*, the mixture of oxide and aluminium powder is ignited by a small cartridge or a strip of magnesium ribbon :

$$Cr_2O_3+2Al\rightarrow 2Cr+Al_2O_3$$
$$3Mn_3O_4+8Al\rightarrow 9Mn+4Al_2O_3$$

The aluminium forms alumina and the temperature rises so high that the alumina fuses, and the metal isolated is obtained in a molten form.

Where the ore is a Sulphide.

Where the ore is some sulphide of contaminated with sulphur or even arsenic, it is first *roasted* in air i.e. heated with oxygen. This converts the metal into oxide, with the removal of sulphur dioxide. The oxide is then reduced for the metal by reduction with carbon or aluminium..

(a) *Zinc blende*, *Zns*, on roasting gives ZnO.

$$2ZnS+3O_2\rightarrow 2ZnO+2SO_2$$

and then ZnO is reduced by carbon :

$$ZnO+C\rightarrow Zn+CO$$

(b) *Galena*, *PbS*, when roasted, is partly converted to PbO and partly to $PbSO_4$, which slightly complicates the process, and therefore, resort is taken to a special treatment in *reverberatory* furnace.

(c) Iron ores are contaminated with sulphur and arsenic and, therefore, they require roasting, before reducing the iron oxide to the metal. Cobalt ore, for example, *cobalt glance* $(CO, Fe)\ AsS$, contains arsenic and sulphur and, therefore, roasting is necessary before other treatments. This gives us a mixture of the oxides of iron, cobalt and sometimes of the contaminated nickel. Their separation is effected by the usual methods.

(d) *Cinnabar*, *HgS*, on roasting in air gives mercury directly :

$$HgS+O_2\rightarrow Hg+SO_2$$

because the metal at this temperature is not readily oxidised.

This process is known as "*Air reduction Process*".

Electrolytic method where the source is a halide.

We have said that the alkali metals generally occur in nature as chlorides. Common salt is sodium chloride, sylvine is pure potassium chloride and carnallite is a double salt of potassium and magnesium. Calcium, barium and strontium, which occur as **carbonates, are also easily converted to halides.**

The alkali metals *Li*, *Na*, *K*, *Rb* and *Cs*, the metals of alkaline earths, *Ca*, *Ba* and *Sr*, and similarly *Mg*, are obtained by electrolysis of their fused chlorides. The salts of these metals being stable do not easily yield to the isolation of metals in other ways.

The addition of potassium chloride to the fused chloride of the metal required, has sometimes facilitated the process of electrolysis.

For electrolysis, a cylindrical iron pot is generally taken and the cathode is usually of iron and the anode of nickel. The results are summarised below—

The fused substance electrolysed	*The metal obtained*
$NaCl+KF$ (flux)	Na
$KCl+CaCl_2$ (carbon electrodes)	K
$CaCl_2+CaF_2$ (flux, 600°C)	Ca
Carnallite, $KCl.\ MgCl_2.\ 6H_2O+CaF_2$ (700°C)	Mg.

The process of electrolysis is very general, it requires the careful choice of electrodes and the regulation of the temperature of fusion. In case where extra potassium or calcium halides are added, the metal obtained is slightly impure, being a mixture of the two metals, these may be separated by careful distillation in vacuo. This process of purification is, however, not effective in some cases.

11.9. Classification of Metallurgical Processes

Metallurgical processes may be divided into three main types :

(i) *Hydrometallurgy*,
(ii) *Pyrometallurgy*,
(iii) *Electrometallurgy*.

(i) *Hydrometallurgy* : Extraction of metals involving aqueous solution is known as Hydrometallurgy. Silver, Gold etc. are obtained using Hydrometallurgical processes.

(ii) *Pyrometallurgy* : Extraction of metals using heat is known as the Pyrometallurgy. It involves concentration of ores, roasting, calcination, smelting, reduction and refining of metals. *Cu*, *Fe*, *Hg*, *Zn*, *Sn*, *Pb* etc. are obtained using Pyrometallurgical processes.

(iii) *Electrometallurgy* : Extraction of metals by electrolysis of fused chlorides or oxides is called electrometallurgy. Highly electropositive metals are obtained by Electrometallurgical processes. *Na*, *K*, *Mg*, *Ca*, *Al* etc. are obtained by this method.

11.10. Metal Extraction Techniques

Metal	Reduction Electrode Potential (volt)	Main source	Main method of Extraction	Equation
Na	−2·71	Rock salt, $NaCl$	Electrolysis of mixture of fused $NaCl$ and CaF_2 (flux)	$M^{n+}+ne^{-1}\to M$ $Na^{+}+e\to Na$
Mg	−2·37	Carnallite $KCl.MgCl_2 6H_2O$ Magnesite $MgCO_3$	Electrolysis of fused carnallite	$Mg^{+2}+2e\to Mg$
Ca	−2·87	Lime stone $CaCO_3$	Electrolysis of fused mixture of $CaCl_2$ and CaF_2	
Al	−1·66	Bauxite $Al_2O_3\,2H_2O$	Electrolysis of Al_2O_3 dissolved in molten cryolite	$Al^{3+}+3e\to Al$
Zn	−0·76	Zinc blende (ZnS) Calamine ($ZnCO_3$) Zincite (ZnO)	Roasting ZnS to ZnO and reducing ZnO with carbon	$ZnO+C\to Zn+CO\uparrow$
Fe	−0·44	Haematite (Fe_2O_3)	Reduction of oxide with CO	$Fe_2O_3+3CO\to 2Fe+3CO_2$
Sn	−0·14	Tin stone or Cassiterite SnO_2	Reduction of SnO_2 with carbon	$SiO_2+2C\to Sn+2CO$
Pb	−0·13	Galena (PbS)	Reduction of PbO with carbon	$PbO+C\to Pb+CO$
Cu	+0·34	Copper pyrite (Cu_2S, Fe_2S_3)	Partial oxidation of Cu_2S to Cu_2O. Reduction of Cu_2O with unchanged Cu_2S.	$2Cu_2S+3O_2\to 2Cu_2O+2SO_2$ $2Cu_2O+Cu_2S\to 6Cu+SO_2$
Hg	+0·785	Cinnabar HgS	Partial thermal oxidation of HgS	$HgS+O_2\to Hg+SO_2$
Au	+1·5	Free state	Cyanide Process	$4Au+8KCN+2H_2O+O_2\to 4K[Au(CN)_2]+4KOH$ $2K[Au(CN)_2]+Zn\to K_2[Zn(CN)_4]+2Au$

11.11. Refining of Metals

Metals obtained as above are usually impure and need purification. Some of the methods used in the refining metals are given below :

(i) *By poling* : The molten metals is stirred with green wood poles. Wood at the high temperature of the molten metals form hydrocarbons like methane which bring about the reduction of any oxide present in the metal. In the case of tin the impurities are oxidised and float on the molten metal as scum which is removed.

(ii) *By liquation* : This process is used for refining easily fusible metals like lead and tin. The impure metal is heated on the slopy hearth of a reverberatory furnace. The metal melts and flows down leaving the impurities behind.

(iii) *By cupellation* : This is a method employed to purify silver containing lead as an impurity. The impure silver is heated in a shallow vessel made of bone-ash under a blast of air. The lead is easily oxidised to powdery lead monoxide. Most of it is carried away by the blast of air. The rest melts and is absorbed by the bone ash cupel. Pure silver is left behind. Silver itself is not oxidised under these conditions.

(iv) *By distillation* : Some metals have very low melting point and soon vaporise on heating while the associated impurities remain in the solid state. Zinc, mercury and arsenic are purified by this method. Vacum distillation gives very pure product and is used in the refining of the metals of IA and IIA.

(v) *By Fractional distillation* : This process is applied for the separation of cadmium from zinc. In the metallurgy of zinc, the metal is invariably associated with cadmium. The impure zinc is mixed with powdered coke and heated when the first portion of the condensate contain cadmium while zinc is obtained in the subsequent portions.

(vi) *By Electrolytic refining* : This is a very convenient method for refining many impure metals. Most of the metals such as copper, silver, gold, zinc and chromium are refined electrolytically. The impure metal is made the anode and a thin sheet of the pure metal, as cathode. A solution of a salt of the metal serves as the electrolyte. On passing an electric current through the electrolyte, the pure metal is deposited on the cathode from the electrolyte. At the same time more ions of the metal enter the electrolyte by oxidation of the anode. The impurities present in the anode either dissolve in the electrolyte or collect as a muddy deposit (anode mud) below the anode. Thus in the electrolytic refining of copper, impurities of iron and zinc are dissolved in the electrolyte and while gold, platinum and silver are left behind as **anode mud**.

(vii) *Van Arkel Method* : This is used for getting ultra-pure metals. The principle involved is to convert the metal to a volatile unstable compound and to subsequently decompose it to give the pure metal. The impurities present should be such as not to be affected. Metals like titanium, zirconium etc. are purified by using this method.

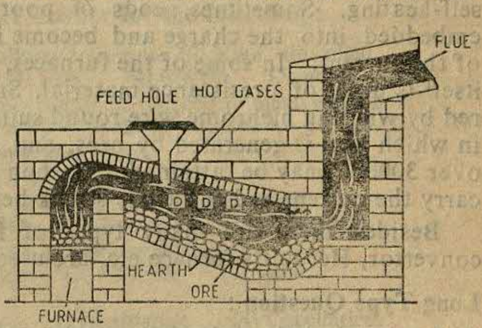
11.12. Furnaces used in Metallurgy

Some of the principal furnaces used are the following :

(i) *Kilns* : These are the structures or enclosures in which the materials are mixed with proper fuel, free access of air is permitted but no fusion takes place. The kilns are sometimes heated by gas or by the waste heat from other furnaces.

(ii) *Blast furnaces* : These are tall structures with gate at the bottom and openings at the top. An air blast is supplied to the furnace by means of bellows, fans or blowing engines through nozzles provided at the bottom; the nozzles are called tuyeres. The materials to be treated are charged into the furnace mixed with the fuel, and as the substances melt, they run down to the bottom and accumulate in the space below the tuyeres known as crucible or hearth. When sufficient material has accumulated into the space a hole is tapped into the furnace and the molten matter is allowed to flow out in a separate receiver. Such blast furnaces are obviously utilised for fusions of reducing character, in which the carbonaceous matter of the fuel acts as the reducing agent. In them the combustion takes place near the region at which the air is blown in, and the ascending stream of gases is cooled by the material in the upper part of the furnace. The extent of cooling depends on the rate of ascent and the height of the column. For reference, *see* metallurgy of iron.

(iii) *Reverberatory furnace* : These are the furnaces in which the fuel is burnt in a separate part of the structure, the flame and hot gases only coming into contact with the material treated. The chamber in these furnaces is horizontal and is divided into two equal parts by a bridge like partition. The smaller part is the fireplace, closed with fire-bars below. The larger portion is the laboratory of the furnace, the bottom of which is known as the bed or hearth. The materials are placed on this bed for treatment. Opposite to the fireplace at the other end, is the fine bridge which communicates with stack or chimney. The root of the furnace gradually takes a bend towards the flue end, and the whole concave bend deflects or reverberates the flame and hot gases from the fire



Reverberatory Furnaces

downward, the roof comprising the concave bend becomes heated and radiates heat on the bed. As the fuel does not come directly in contact with the material, the reverberatory furnace can be utilised both for reduction and oxidation processess. If reduction be desired, the material is mixed with a reducing agent (see metallurgy of tin and lead): and if oxidation, air is blown in. Thus calcination and roasting may also be carried in such furnaces.

(iv) *Muffle furnaces* : It is sometimess desired for certain reasons to exclude the products of combustion as well as the fuel and this is accomplished in muffle furnaces. The muffle is a chamber surrounded by the fire, or by flues through which the products of combustion and hot gases from the fire pass. (For details see extraction of zinc.) These furnaces are used for annealing and gold and silver assaying.

(v) *Regenerative furnaces* : The heat carried away to the flues by the escaping gases is again utilised in these furnaces. A flowing column of air is heated by the hot flue gases, the air is then brought back to the fire and returned to the furnace. This means an economy of fuel. Most of the furnaces are fitted up with regenerative systems.

(vi) *Electric furnaces* : Such furnaces are largely used where cheap power is available, and very high temperatures are required, and also for electrolytic reductions. The furnaces may be classified as (a) *Induction furnaces*, in which the charge lying on the furnace bed or in a crucible constitutes the secondary coil of an induction unit, and the induced currents produced by making and breaking the primary circuit, heat up the material, (b) *Resistance furnaces* in which the heat generated by resistance in the circuit is utilised. Sometimes the material forming the charge acts as the resistance and becomes self-heating. Sometimes, eods of poorly conducting materials are embedded into the charge and become intensely hot on the passage of the current. In some of the furnaces, the body of the furnace itself is made of a resistance material. Small furnaces may be prepared by winding nichrome wire round suitable tubes, (c) *Arc furnaces*, in which heat is generated by arcs, and thereby, a temperature of over 3000°C may be attained. Carbon electrodes are employed to carry the current and the arc is struck between them and the charge.

Besides there are many types of furnaces such as Bessemer convertor, Heroult's furnace etc. are used in metallurgy.

Long Type Question :

1. By what physical and chemical properties can metals be distinguished from non-metals ? (M. U. 1963 A; P. U. '80 A)
   Use them to show that sodium, calcium, zinc and mercury are metals and sulphur and carbon are non-metals. (R. U. 1964 A; B. U. '58 A)
2. How do metals occur in nature ? Illustrate with examples.
   What is the difference between minerals and ores ? (P. U. 1970 A)
3. By what different methods are metals extracted from naturally occurring compounds ? Give briefly one example of each of the above methods from actual commercial processes used for extraction.
   (P. U. 1969 S, '70 A; R. U. '67 S; B.U. '66 A)

4. Describe briefly how a metal may be isolated from its sulphide ores. (P. U. 1980)
   What is meant by the terms Gangue, Flux and Slag ?
5. Distinguish between :
   (a) Ores and Minerals.
   (b) Calcination and Roasting. (B I E C 1983)
   (c) Roasting and Smelting.
   (d) Flux and Slag.
   (e) Slag and Gangue. (Bhag U. 1965 S)
   (f) Alloy and Amalgam. (I. I. T. 1978)
6. Explain the terms : (a) Pyrometallurgy, (b) Hydrometallurgy and (c) Electrometallurgy.
7. What do you understand by the terms : (a) roasting, (b) calcination, (c) smelting ?
   Describe two methods for the refining of metals.
8. Describe different steps involved in the extraction of a metal from, (a) Sulphide ore, (b) Halide ore.
9. Describe different methods used for the refining of metals.
10. Write notes on (a) Blast furnace, (b) Reverberatory furnace, (c) Muffle furnance, (d) Electro-refining (B. I. E. C. 1983), (e) concentration of ores by different methods (B. I. E. C. 1984), (f) use of carbon-reduction process in the extraction of metals with examples. (B. I. E. C. 1984)
11. **Match A with B.**

Metals (A)	*(B) Methods of Extraction*
(i) Zinc	(a) Hydrometallurgy
(ii) Copper	(b) Electrometallurgy
(iii) Silver	(c) Pyrometallurgy
(iv) Calcium	

12. Give reasons for the following :
   (a) Zinc is obtained by carbon-reduction process.
   (b) Al is obtained by electrolytic process.
   (c) Au is obtained by cyanide process.

Select and write the Correct Answer for the following :

13. The substance used in metallurgy to remove silica ete. are called
   (1) Gangue (2) Slag (3) Flux (4) Matrix (5) none.
14. Which of the following oxides cannot be reduced to metal by carbon ?
   (1) HgO (2) CuO (3) Fe_2O_3 (4) Al_2O_3 (5) PbO_2. (P. M. D. T. 1978)
15. Which of the following is an acidic oxide ?
   (1) Na_2O (2) Fe_2O_3 (3) CO_2 (4) CaO.
16. Which of the following is a carbonate ore of Magnesium ?
   (1) Epsomite (2) Carnalite (3) Kesserite (4) Magnesite.
17. Which of the following ore of Al contains fluorine ?
   (1) Bauxite (2) Corundum (3) Cryolite (4) Mica.
18. Silver is purified by :
   (1) Liquation (2) Poling (3) Distillation (4) Cupellation.
19. Which of the following is a liquid metal at R. T. P. ?
   (1) Na (2) Cu (3) Fe (4) Al (5) Hg.
20. Siderite is an ore of :
   (1) Cu (2) Al (3) Ag (4) Fe (5) Zn.
21. Which of the following metal is extracted by electrometallurgy ?
   (1) Cu (2) Zn (3) Na (4) Al (5) More than one.

□□□

CHAPTER 12

COMPOUNDS OF METALS

Metals form compounds like oxides, hydroxides, carbonates, bicarbonates, halides, sulphides, sulphites, sulphates, nitrites and nitrates etc. The general methods of preparation and general properties of the compounds of metals are discussed below.

Oxides of Metals

Preparation :

(i) *By burning the metal in air or oxygen* e.g. :

$$4Na + O_2 \rightarrow 2Na_2O$$
$$2Cu + O_2 \rightarrow 2CuO$$
$$2Zn + O_2 \rightarrow 2ZnO$$

(ii) *By the action of heat on the hydroxides of metals* e.g. :

$$Cu(OH)_2 \rightarrow CuO + H_2O$$
$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$$

(iii) *By the action of steam over red hot metals* e.g. :

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2\uparrow$$

(iv) *By heating metal carbonates* : All metal carbonates except those of the **alkali metals,** are decomposed by heat yielding the oxide and carbon dioxide e.g.

$$CaCO_3 \rightarrow CaO + CO_2; \; ZnCO_3 \rightarrow ZnO + CO_2$$

(v) *By heating metal nitrates* : Nitrates of heavy metals lose nitrogen peroxide and oxygen leaving their oxide e.g.

$$2M(NO_3)_2 \rightarrow 2MO + 4NO_2 + O_2 \; (M = Cu, Hg, Pb)$$

(vi) *By heating sulphates of metals* : All metal sulphates except **alkali sulphates** on heating give metal oxides.

$$2FeSO_4 \rightarrow Fe_2O_3 + SO_2 + SO_3$$
$$PbSO_4 \rightarrow PbO + SO_3$$

(vii) *By heating sulphides of metals* in air.

$$2MS + 3O_2 \rightarrow 2MO + 2SO_2 \; (M = Zn, Cu, Pb)$$

(viii) *By the action of Caustic soda or Potash on some metal compounds* :

$$2AgNO_3 + 2NaOH \rightarrow Ag_2O + 2NaNO_3 + H_2O$$
$$HgCl_2 + 2NaOH \rightarrow HgO + 2NaCl + H_2O$$

Properties of Metal oxides :

(i) *Nature* : Metal oxides are generally basic in nature except ZnO, SnO, Al_2O_3 etc. which are amphoteric.

(ii) *Action of water* : (a) Oxides of *Na*, *K* and *Ca* react with water at ordinary temperatures forming their hydroxides.

$$Na_2O+H_2O \rightarrow 2NaOH$$
$$Na_2O_2+2H_2O \rightarrow 2NaOH+O_2$$

(a) *MgO* forms $Mg(OH)_2$ on boiling with water.

$$MgO+H_2O \rightarrow Mg(OH)_2$$

Other metal oxides do not dissolve in water.

(iii) *Action of acids* : Oxides of metals are generally basic in nature, hence they react with acids to form salt and water.

$$CuO+H_2SO_4 \rightarrow CuSO_4+H_2O$$
$$MgO+2HCl \rightarrow MgCl_2+H_2O$$

(iv) *Action of alkalis* : Some metallic oxides react with both acids and bases. They are called amphoteric oxides. These oxides are Al_2O_3, ZnO, SnO etc.

$$ZnO+2NaOH \rightarrow Na_2ZnO_2 \text{ (Sod. Zincate)}+H_2O$$
$$SnO+2NaOH \rightarrow Na_2SnO_2 \text{ (Sod. Stannite)}+H_2O$$
$$Al_2O_3+2NaOH \rightarrow 2NaAlO_2 \text{ (Sod. Aluminate)}+H_2O$$

HYDROXIDES OF METALS

Preparation :

(i) *By the action of water on active metals* :

$$2M+2H_2O \rightarrow 2MOH+H_2 \ (M=Na,\ K)$$
$$Ca+2H_2O \rightarrow Ca(OH)_2+H_2$$

(ii) *By the action of water on metal oxides* :

$$Na_2O+2H_2O \rightarrow 2NaOH$$
$$CaO+H_2O \rightarrow Ca(OH)_2$$

(iii) *By the action of MOH* ($M=Na,\ K,\ NH_4^+$) *on the aqueous salt solutions* :

$$CuSO_4+2NaOH \rightarrow Cu(OH)_2\downarrow+Na_2SO_4$$
$$FeCl_3+3NH_4OH \rightarrow Fe(OH)_3\downarrow+3NH_4Cl$$

Properties :

(i) *Action of water* : Alkali metal hydroxides are extremely soluble in water. The hydroxides of the alkaline earth metals are sparingly soluble in water. The hydroxides of all other metals are mostly insoluble in water.

(ii) *Action of heat* : Hydroxides of alkali metals simply melt on heating without any chemical change, the others all lose water forming oxides.

$$Ca(OH)_2 \rightarrow CaO+H_2O; \ 2Al(OH)_3 \rightarrow Al_2O_3+3H_2O$$

(iii) *Action of acids* : They form salts and water with acids.

$$M(OH)_2+H_2SO_4 \rightarrow MSO_4+2H_2O \ (M=Zn,\ Mg,\ Ca,\ Ba,\ Cu)$$

(iv) *Action of alkalis* : Hydroxides of Zn, Al and Sn (amphoteric metals) react with $NaOH$ or KOH forming salts.

$$Zn(OH)_2+2NaOH \rightarrow Na_2ZnO_2+2H_2O$$
$$Al(OH)_3+NaOH \rightarrow NaAlO_2+2H_2O$$

CARBONATES OF METALS

Preparation :

(i) *By the action of CO_2 on solution of metal hydroxides* :

$$Ca(OH)_2+CO_2 \rightarrow CaCO_3+H_2O$$
$$2NaOH+CO_2 \rightarrow Na_2CO_3+H_2O$$

When excess of CO_2 is passed, these carbonates are converted into their bicarbonates.

$$Na_2CO_3+H_2O+CO_2 \rightarrow 2NaHCO_3$$
$$CaCO_3+H_2O+CO_2 \rightarrow Ca(HCO_3)_2$$

(ii) *By the action of heat on bicarbonates* :

$$M(HCO_3)_2 \rightarrow MCO_3+H_2O+CO_2 \ (M=Zn, Cu, Ca)$$
$$2NaHCO_3 \rightarrow Na_2CO_3+H_2O+CO_2$$

(iii) *By the action of Na_2CO_3, K_2CO_3 or $(NH_4)_2CO_3$ on aqueous solutions of salts.*

(a) *Normal carbonates* :

$$MCl_2+Na_2CO_3 \rightarrow MCO_3\downarrow+2NaCl \ (M=Ca^{+2}, Sr^{+2}, 2Ba)$$

(b) *Basic carbonates* : Salts of Zn, Cu, Pb, Mg etc. produce basic carbonates e.g.

$$2M(NO_3)_2+2Na_2CO_3+H_2O \rightarrow M(OH)_2.MCO_3\downarrow+CO_2+4NaNO_3 \quad (M=Zn, Cu, Pb, Mg)$$

Normal carbonates of these metals are generally prepared by the action of $NaHCO_3$ solution on aqueous solutions of salts.

$$ZnCl_2+2NaHCO_3 \rightarrow ZnCO_3\downarrow+H_2O+2NaCl+CO_2$$

Properties :

(i) All metal carbonates excepting Na_2CO_3, K_2CO_3, $(NH_4)_2CO_3$ are insoluble in water.

(ii) *Action of heat* : All metal carbonates except Na_2CO_3 and K_2CO_3 decompose into oxides on heating.

$$MCO_3 \rightarrow MO+CO_2\uparrow \ (M=Ca, Zn, Cu \text{ etc.})$$

(iii) *Action of acids* : Carbonates dissolve in acids forming salts and CO_2 gas is evolved (effervescence).

$$Na_2CO_3+H_2SO_4 \rightarrow Na_2SO_4+CO_2\uparrow+H_2O$$
$$CaCO_3+2HCl \rightarrow CaCl_2+CO_2\uparrow+H_2O$$

CHLORIDES OF METALS

Preparation :

(i) *By the combination of metal and chlorine* :

$$2Na+Cl_2 \rightarrow 2NaCl; \ Ca+Cl_2 \rightarrow CaCl_2$$

(ii) *By passing dry HCl gas over hot metal* :

$$Fe+2HCl \rightarrow FeCl_2+H_2\uparrow$$

(iii) *By dissolving metals into hydrochloric acids* :

$$M+2HCl \rightarrow MCl_2+H_2 \ (M=Mg, Zn, Fe)$$

(iv) *By the action of hydrochloric acid on metal oxides, hydroxides, carbonates and sulphides* :

$$CuO+2HCl \rightarrow CuCl_2+H_2O$$
$$CaCO_3+2HCl \rightarrow CaCl_2+H_2O+CO_2$$
$$Fe(OH)_2+2HCl \rightarrow FeCl_2+2H_2O$$
$$FeS+2HCl \rightarrow FeCl_2+H_2S$$

(v) *By treating aqueous solution of the another salt of the metal with the aqueous solution of a chloride* e.g.

$$AgNO_3+NaCl \rightarrow AgCl\downarrow+NaNO_3$$

Properties :

(i) *Action of water* : All metal chlorides are soluble in water except Cu_2Cl_2, Hg_2Cl_2, $AgCl$ and $PbCl_2$. But $PbCl_2$ is soluble in hot water.

(ii) *Action of heat* : The chlorides except those of the noble metals are stable to heat. Hydrated chlorides lose their water of crystallisation on heating. Some chlorides volatilize out e.g. Hg_2Cl_2 and some decompose on heating e.g.

$$2MgCl_2.6H_2O \rightarrow Mg_2OCl_2+5H_2O+2HCl$$
$$2CuCl_2.2H_2O \rightarrow Cu_2Cl_2+Cl_2+4H_2O$$

SULPHIDES OF METALS

Preparation :

(i) *By heating metals with sulphur* :

$$Fe+S \rightarrow FeS$$

(ii) *By reducing sulphates of metals with carbon* :

$$BaSO_4+4C \rightarrow BaS+4CO\uparrow$$

(iii) *By reducing sulphates of metals with hydrogen* :

$$BaSO_4+4H_2 \rightarrow BaS+4H_2O$$

(iv) *By heating a mixture of the oxide with carbon and sulphur* :

$$Al_2O_3+3C+3S \rightarrow Al_2S_3+3CO\uparrow$$

(v) *By passing H_2S to the aqueous solution of salts* :

(a) *In acid medium*, the following salts give precipitate with H_2S gas.

$$M(NO_3)_2+H_2S \rightarrow \underset{\text{Black}}{MS\downarrow}+2HNO_3 \ (M=Cu^{2+}, Pb^{2+}, Hg^{2+})$$

(b) *In ammoniacal medium* (NH_4OH) : H_2S gas gives precipitate with the following salts :

$$M(NO_3)_2+H_2S \rightarrow \underset{\text{Black}}{MS\downarrow}+2HNO_3 \ (M=Ni^{+2}, Co^{2+})$$

$$ZnSO_4+H_2S \rightarrow \underset{\text{White}}{ZnS\downarrow}+H_2SO_4$$

Properties :

(i) *Action of heat* : On heating in air, sulphides are usually oxidised to metallic oxide and sulphur dioxide.

$$2ZnS+3O_2\rightarrow 2ZnO+2SO_2$$

Sometimes, the metal is formed.

$$HgS+O_2\rightarrow Hg+SO_2\uparrow$$

(ii) *Action of acids* : Sulphides produce H_2S on treatment with acids :

$$ZnS+2HCl\rightarrow ZnCl_2+H_2S$$
$$FeS+H_2SO_4\rightarrow FeSO_4+H_2S$$

(iii) *Solubility in water* : All metal sulphides are insoluble in water except sulphides of alkali metals. Sulphides of *Ca*, *Mg*, *Al*, *Ba* etc. produce H_2S with water.

$$MgS+2H_2O\rightarrow Mg(OH)_2+H_2S.$$

SULPHATES OF METALS

Preparation :

(i) *By the action of dilute H_2SO_4 on metals :*

$$M+H_2SO_4\rightarrow MSO_4+H_2\ (M=Mg, Zn, Fe)$$

(ii) *By the action of conc. H_2SO_4 on metals below hydrogen in the electrochemical series :*

$$M+2H_2SO_4\rightarrow MSO_4+SO_2+2H_2O\ (M=Hg, Cu)$$

(iii) *By the action of dil. H_2SO_4 on metal oxides, hydroxides, carbonates and sulphides :*

$$CuO+H_2SO_4\rightarrow CuSO_4+H_2O$$
$$Fe(OH)_2+H_2SO_4\rightarrow FeSO_4+2H_2O$$
$$ZnCO_3+H_2SO_4\rightarrow ZnSO_4+H_2O+CO_2$$
$$FeS+H_2SO_4\rightarrow FeSO_4+H_2S$$

(iv) *By the action of hot concentrated sulphuric acid on a salt of a more volatile acid :*

$$2NaCl+H_2SO_4\rightarrow Na_2SO_4+2HCl$$
$$2KNO_3+H_2SO_4\rightarrow K_2SO_4+2HNO_3$$

(v) *By the action of soluble sulphate on the aqueous solution of the salt :*

$$BaCl_2+Na_2SO_4\rightarrow BaSO_4\downarrow+2NaCl$$

(vi) *By burning metal sulphides in air or oxygen :*

$$ZnS+2O_2\rightarrow ZnSO_4$$

Properties :

(i) All metal sulphates are soluble in water except $CaSO_4$, $BaSO_4$, $PbSO_4$ and $SrSO_4$. Sulphates of *Ag* and *Hg* (ous) are little soluble. $BaSO_4$ is the most insoluble sulphate among the insoluble one.

(ii) *Action of heat* : On heating, the hydrated sulphates lose their water of crystallisation. All sulphates decompose on heating except alkali metal sulphates which are most stable.

$$ZnSO_4.7H_2O \rightarrow 7H_2O + ZnSO_4 \xrightarrow{\text{heat}} ZnO + SO_3$$

Exception : (a) $Na_2SO_4.10H_2O \rightarrow Na_2SO_4 + 10H_2O$

↓ heat

no change

(b) $$FeSO_4.7H_2O \rightarrow 7H_2O + FeSO_4 \xrightarrow{\text{heat}} Fe_2O_3 + SO_2 + SO_3$$

NITRATES OF METALS

Preparation :

(i) *By the action of nitric acid on metals* :

$$Mg + 2HNO_3 \text{ (very dil)} \rightarrow Mg(NO_3)_2 + H_2$$

$$Cu + 4HNO_3 \text{ (conc.)} \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

(ii) *By the action of nitric acid on metals oxides, hydroxides or carbonates* :

$$CuO + 2HNO_3 \rightarrow Cu(NO_3)_2 + H_2O$$

$$CuCO_3 + 2HNO_3 \rightarrow Cu(NO_3)_2 + H_2O + CO_2\uparrow$$

Properties :

(i) *Solubility in water* : All nitrates of metals are soluble in water.

(ii) *Action of heat* : (a) Alkali nitrates melt on heating and lose oxygen to form corresponding nitrites.

$$2MNO_3 \rightarrow 2MNO_2 + O_2 \ (M = Na, K)$$

(b) Nitrates of heavy metals lose nitrogen peroxide and oxygen forming the oxide.

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

(c) Mercury and Silver nitrate are converted into the metals on heating respectively :

$$2AgNO_3 \rightarrow 2Ag + 2NO_2 + O_2$$

$$Hg(NO_3)_2 \rightarrow Hg + 2NO_2 + O_2$$

(iii) *Metallic nitrates produce ammonia on heating with zinc and sodium hydroxide* :

$$\begin{array}{l} Zn + 2NaOH = Na_2ZnO_2 + 2\text{'}H\text{'} \ [\times 4] \\ \underline{NaNO_3 + 8\text{'}H\text{'} = NaOH + NH_3 + 2H_2O} \\ 4Zn + 7NaOH + NaNO_3 \rightarrow 4Na_2ZnO_2 + NH_3 + 2H_2O \end{array}$$

QUESTIONS

Long and Short Types :

1. Discuss some general methods of preparation of metal oxides. Describe the action of :

(a) heat, (b) water, (c) acids and, (d) bases on metal oxides.

2. Describe some general methods of preparing :

(a) carbonates of metals, (b) nitrates of metals and, (c) chlorides of metals. Discuss the action of heat on (a) metal carbonates, (b) metal nitrates.

3. What happens when :

(a) Sodium carbonate is strongly heated, (b) Sodium nitrate is strongly heated, (c) Lead nitrate is heated, (d) $Al_2(SO_4)_3$ reacts with excess of $NaOH$ solution ?

4. Discuss the effect of heat on the following :

(a) Metal hydroxides, (b) Metal sulphates, (c) Metal nitrates, (d) Metal carbonates.

5. Discuss the solubility of the following compounds in water :

(a) Metal oxides, (b) Metal hydroxides, (c) Metal carbonates, (d) Metal nitrates, (e) Metal chlorides.

6. **Fill up the blank :**

(a) ZnO is————in nature. (b) Hydroxides of all metals except those of the alkali and the alkaline earth metals are————in water. (c) All nitrates are————in water. (d) On strong heating, copper nitrate produces NO_2 and O_2. (e) On heating KNO_3 forms————and oxygen. (f) $FeSO_4$ is————in water.

Select and write the correct answer for the following :

7. Na_2CO_3 is (1) soluble in water, (2) insoluble in water, (3) sparingly soluble in water, (4) None of these.

8. $NaNO_3$ on heating gives (1) Na_2O, (2) $NaNO_2$ and O_2, (3) Na_2O_2 and NO_2, (4) Na_2O and N_2.

9. When sodium nitrate is heated with Zn and $NaOH$ solution then which of the following gas is obtained ?

(1) N_2O, (2) NH_3, (3) H_2, (4) NO, (5) NO_2.

10. When hydrated magnesium chloride is heated then which of the following is obtained ?

(1) Anhyd. $MgCl_2$, (2) Mg_2OCl_2, (3) $MgCl_2H_2O$, (4) MgO, (5) None.

11. Which of the following sulphate does not decompose on heating ?

(1) $CuSO_4$, (2) $FeSO_4$, (3) Na_2SO_4, (4) $CaSO_4$.

12. Which of the following is an amphoteric oxide ?

(1) CaO, (2) MgO, (3) CuO, (4) ZnO.

□□□

CHAPTER 13

STUDY OF SODIUM

Sodium

Symbol : *Na*, *At. No.* 11, *At. Wt.* 23,

Electronic configuration : $1s^2, 2s^2 2p^6, 3s^1$

Occurrence : It always occurs as its compounds. Important sources of sodium are : (i) common salt ($NaCl$), (ii) Chile salt petre ($NaNO_3$) and (iii) Borax ($Na_2B_4O_7.10H_2O$).

Extraction of Sodium :

Extraction of sodium metal is carried out by the electrolysis of fused caustic soda (Castner's Process) or fused sodium chloride (Down's process).

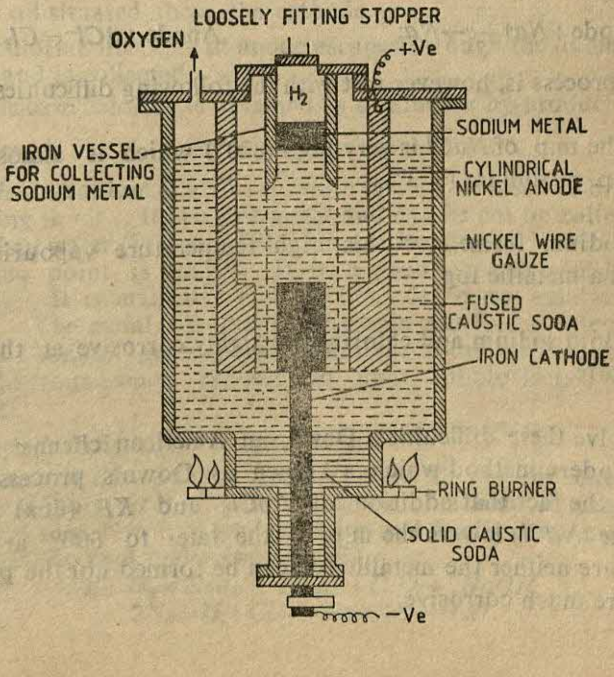
(a) **Castner's Process** : In this process, fused caustic soda is electrolysed. The following electrolytic reactions take place on passing an electric current through the electrolyte.

$$NaOH \rightleftharpoons Na^+ + OH^-$$

Hydroxyl ions are unstable in molten hydroxide and decompose to give O^{-2} and H^+ ions.

$$OH^- \rightleftharpoons O^{-2} + H^+$$

The sodium and hydrogen ions travel towards the cathode and



the oxygen ions towards the anode. The following reactions take place at the electrodes.

At the cathode : $Na^+ + e \rightarrow Na$

$2H^+ + 2e \rightarrow H_2$

At the anode : $2O^{-2} \rightarrow O_2 + 4e$

Sodium metal is liberated at the cathode and being lighter than fused caustic soda collects at its surface. It is collected from time to time with the help of a nickel perforated ladle. Hydrogen gas evolved at the cathode provides a reducing atmosphere and prevents the oxidation of sodium. Oxygen evolved at the anode is not allowed to mix with sodium and hydrogen produce at the cathode.

(b) **Down Process** : This is the modern process for the extraction of sodium. It is more economical than Castner's process because of lesser consumption of electricity and because sodium chloride is cheaper than sodium hydroxide.

Principle : In this process sodium is obtained by electrolysis of fused sodium chloride.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

Cathode : $Na^+ + e \rightarrow Na$; Anode : $2Cl^- \rightleftharpoons Cl_2 + 2e$

The process is, however met with the following difficulties :

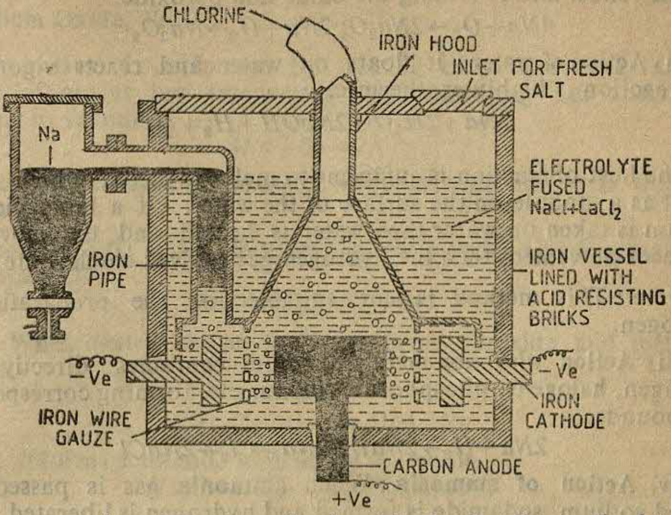
(i) The m.p. of $NaCl$ is very high (820°) which is almost equal to the b.p. of sodium (883°).

(ii) Sodium formed at this high temperature vapourises and produces a metallic fog.

(iii) Both sodium and chlorine are highly corrosive at this high temperature.

To solve these difficulties, Down, an American chemist in 1924 gave a modern method which is known as Down's process. It is based on the fact that addition of $CaCl_2$ and KF (flux) to the electrolyte ($NaCl$) lowers the m.p. of the later to 600° at which temperature neither the metallic fog can be formed nor the products formed are much corrosive.

Description : The cell used by Down is given below :



It consists of an iron box lined with fire-bricks (cathode). A graphite rod rises through the bottom and is made anode. It is surrounded by cylindrical iron cathode, the two being separated by a wire gauze partition. Sodium liberated at the cathode, being lighter than fused sodium chloride. flows into a receiver containing kerosene oil situated above the cathode.

The chlorine liberated at anode escapes through the dome-shaped receiver and is collected.

In this case chlorine is obtained as a valuable by-product.

Properties :

Physical : Sodium is a silvery white metal. It loses its brightness on keeping in air. It is a soft metal and can be cut by knife. It is lighter than water (Sp. gr. 0·97). Its melting point is 97·5°C and its boiling point is 882°C. It is a good conductor of heat and electricity. It is malleable and ductile. It forms amalgam with mercury. The metal dissolves in ammonia and forms intense blue solution. Sodium gives purple colloidal solution in ether. It emits electrons when exposed to light (photoelectric electron emission).

Chemical : It is highly reactive metal.

(i) **Action of air** : Sodium is quite stable in dry air but readily tarnishes in moist air due to the formation of a film of the monoxide which soon changes into hydroxide and finally into carbonate. It is, therefore, kept under *kerosene oil* :

$$4Na+O_2 \rightarrow 2Na_2O;\; Na_2O+H_2O \rightarrow 2NaOH$$
$$2NaOH+CO_2 \rightarrow Na_2CO_3+H_2O$$

On heating the metal in air or oxygen it burns with a brilliant golden yellow flame forming the oxide and peroxide.

$$4Na+O_2\rightarrow 2Na_2O;\ 2Na+O_2\rightarrow Na_2O_2$$

(ii) Action of water : It floats on water and reacts vigorously. The reaction is highly exothermic.

$$2Na+2H_2O\rightarrow 2NaOH+H_2+Q$$

The heat of reaction is sufficient to melt the metal, which swims about as a globule on the surface of the water. If a large piece of sodium is taken on water then water is heated and the movement of pieces prevented, then the hydrogen gas evolved catches fire.

Note : This method is not suitable for the preparation of hydrogen.

(iii) Action with non-metals : Sodium combines directly with hydrogen, halogens, phosphorus, sulphur etc. forming corresponding compounds.

$$2Na+H_2\rightarrow 2NaH;\ 2Na+Cl_2\rightarrow 2NaCl$$

(iv) Action of ammonia : When ammonia gas is passed over heated sodium, sodamide is formed and hydrogen is liberated.

$$2Na+2NH_3\xrightarrow{300\text{-}400°C}2NaNH_2+H_2\uparrow$$

(v) Action of alcohols : Sodium dissolves much more quickly in ethyl alcohol forming H_2.

$$2C_2H_5OH+2Na\rightarrow \underset{\text{Sod. ethoxide}}{2C_2H_5ONa}+H_2\uparrow$$

(vi) Action with mercury : With mercury sodium forms amalgam of varying composition :

$NaHg$ and Na_3Hg etc.

(vii) Action with acids : It reacts violently with acid evolving hydrogen.

$$2Na+2HCl\rightarrow 2NaCl+H_2;\ 2Na+H_2SO_4\rightarrow Na_2SO_4+H_2\uparrow$$

(viii) Action of alkyl halides (Wurtz reaction) : When an ethereal solution of an alkyl halide is treated with sodium an alkane is formed.

$$2R-X+2Na\xrightarrow{\text{Ether}}R-R+2NaX,\ \text{where } R=CH_3,\ C_2H_5,\ C_3H_7 \text{ etc.}$$

(ix) As reducing agent : Sodium has great affinity for oxygen and halogens and as such it acts as a powerful reducing agent.

$$Al_2O_3+6Na\rightarrow 3Na_2O+2Al;\ 3CO_2+4Na\rightarrow 3C+Na_2CO_3.$$

Uses : (i) In the manufacture of Na_2O_2, $NaCN$, $NaNH_2$; (ii) as a reagent in organic chemistry; (iii) in the extraction of Mg, B, Si; (iv) in photo electric cell; (v) for the production of artificial rubber, dyes, drugs and perfumes.

13.1. Compounds of Sodium

1. Sodium Oxide, Na_2O.

Preparation : It is formed by heating the metal in a limited supply of air at low temperature and removing the metal by distilling in vacuum.

$$4Na+O_2\rightarrow 2Na_2O$$

The oxide so obtained is mixed with peroxide which is difficult to separate.

Properties : (i) It is a white amorphous powder which react with water violently.

$$Na_2O+H_2O\rightarrow 2NaOH$$

(ii) When heated above 400°C it forms peroxide and metallic sodium.

$$2Na_2O\xrightarrow{400^\circ}Na_2O_2+2Na.$$

(iii) It forms sodamide with liquid ammonia.

$$Na_2O+NH_3\rightarrow NaNH_2+NaOH$$

2. Sodium Peroxide, Na_2O_2.

Preparation :

It is formed along with monoxide when sodium is heated to 350°C in the excess of air or oxygen (free from carbon dioxide).

$$2Na+O_2\rightarrow Na_2O_2$$

Properties : (i) It is a yellow substance which when exposed to air turns white due to the formation of $NaOH$ and Na_2CO_3.

$$2Na_2O_2+2H_2O\rightarrow 4NaOH+O_2$$
$$2NaOH+CO_2\rightarrow Na_2CO_3+H_2O$$

(ii) With cold water it forms caustic soda and hydrogen peroxide but with warm water oxygen is evolved.

$$Na_2O_2+2H_2O\xrightarrow{\text{cold}}2NaOH+H_2O_2$$
$$2Na_2O_2+2H_2O\xrightarrow{\text{warm}}4NaOH+O_2$$

(iii) It reacts with dil. acids as follows :

(a) $$Na_2O_2+2HCl\xrightarrow{\text{cold}}2NaCl+H_2O_2$$

(b) $$Na_2O_2+4HCl\xrightarrow{\text{hot}}4NaCl+2H_2O+O_2$$

(iv) It decomposes nitrous oxide and nitric oxide on heating.

$$Na_2O_2+2N_2O\rightarrow 2NaNO_2+N_2$$
$$Na_2O_2+2NO\rightarrow 2NaNO_2$$

(v) **As an oxidising agent** : It is a powerful oxidising agent and oxidises chromium salts into chromates, manganese salts to manganates, SO_2 to SO_3 and iron chromite ($FeCr_2O_4$) and iron pyrites (FeS_2) to ferric oxide.

$$2Cr(OH)_3+3Na_2O_2\rightarrow 2Na_2CrO_4+2NaOH+2H_2O$$
$$2Mn(OH)_2+4Na_2O_2\rightarrow 2Na_2MnO_4+4NaOH$$
$$2FeCr_2O_4+5Na_2O_2\rightarrow Fe_2O_3+2Na_2CrO_4+3Na_2O+2O_2$$
$$2FeS_2+15Na_2O_2\rightarrow Fe_2O_3+4Na_2SO_4+11Na_2O$$

Uses : (i) As an oxidising agent in the laboratory.

(ii) For purifying air in submarines, hospitals etc.

$$2Na_2O_2+CO_2\rightarrow 2Na_2CO_3+O_2$$

(iii) For bleaching silk, wool etc.

(iv) In the manufacture of benzoyal peroxide, dyes and other organic compounds of commercial use.

3. Sodium Hydride, NaH.

Preparation : It is obtained by heating sodium in a current of hydrogen at 370°C.

$$2Na+H_2\xrightarrow{370°C}2NaH$$

Properties :

(i) It is a crystalline powder and evolves hydrogen with water.

$$NaH+H_2O\rightarrow NaOH+H_2\uparrow$$

(ii) When sodium hydride is electrolysed, H_2 is evolved at the anode.

$$NaH\rightleftharpoons Na^++H^-$$

Anode $2H^-\rightarrow H_2+2e$

Cathode $Na^++e\rightarrow Na$

(iii) It combines with CO_2 to form sodium formate.

$$NaH+CO_2\rightarrow HCOONa$$

4. Sodium hydroxide (Caustic soda), $NaOH$:

It is an important chemical and is manufactured on large scale. At present there are 25 units working in India producing about 22 million tons annually. It is manufactured by the following three methods :

1. Soda Lime Process : (Causticisation Process) or Cossage Process :

In this process milk of lime is added to hot sodium carbonate solution when sodium hydroxide is obtained along with sparingly soluble calcium carbonate.

$$Na_2CO_3+Ca(OH)_2\rightarrow 2NaOH+CaCO_3\downarrow$$

2. Electrolytic Process : It is based on electrolysis of sodium chloride solution whereby sodium liberated at cathode reacts with water to form hydroxide.

$$NaCl \xrightarrow{\text{Electrolysis}} Na^+ + Cl^-$$

Cathode $Na^+ + e \rightarrow Na$

$$Na + Hg \rightarrow Na/Hg$$

$$2Na/Hg + 2H_2O \rightarrow 2NaOH + H_2 + 2Hg$$

Anode $2Cl^- \rightarrow Cl_2 + 2e$

But the process is met with the *following difficulties* :

(i) Cl_2 liberated at anode reacts readily with $NaOH$ liberated at cathode even in cold to form $NaCl$ and $NaClO$.

(ii) Cl_2 forms an explosive mixture with H_2.

It is thus essential that the electrolytic cell should be constructed in such a way that the reaction products are not allowed to come in contact with one another. To achieve this, different types of cells are used, the most common of which are :

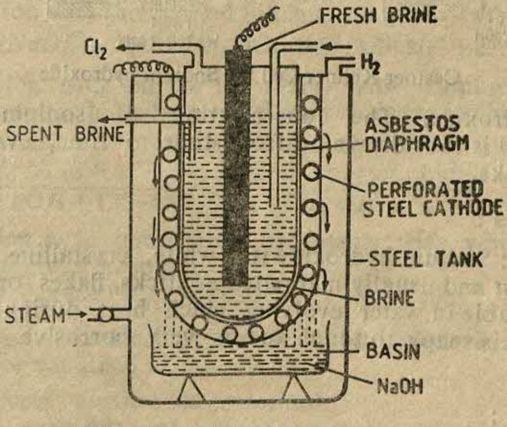
A. Nelson's Cell : It consists of :

Cathode : Perforated U-shaped steel tube lined inside with porous diaphragm of asbestos.

Anode : Carbon rod.

Electrolyte : Saturated $NaCl$ solution.

The whole cell is suspended in iron tank. On passing an electric current Cl_2 is evolved at anode while Na^+ ions due to electrostatic pull of cathode (−ve pole) pass through asbestos, change to sodium atom at cathode and react with *steam* to form sodium hydroxide solution.



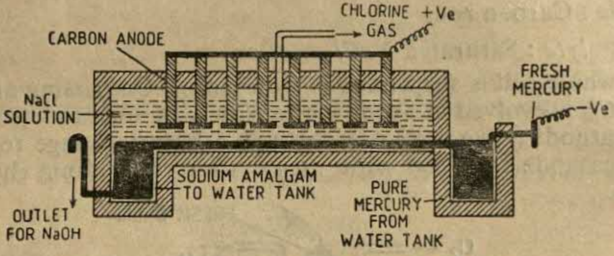
Nelson's cell for Sodium hydroxide.

It collects at the bottom of the tank, and is drawn out from time to time, concentrated and evaporated into solid flakes. H_2 and Cl_2 are obtained as by-products.

B. Castner Kellner Cell :

It consists of a rectangular tank divided into three compartments by slate partitions. These slate partitions do not touch the bottom of the cell, but fit into groves at the bottom. The bottom is covered with a layer of mercury. The cell is pivoted at one end and rests on an eccentric wheel '*H*' at the other end. The central compartment contains dilute solution of *NaOH* in which are suspended number of *iron rods* acting as *cathode*. The outer compartments, however contain *NaCl* solution and *carbon rods* acting as *anode*. The layer of mercury acts as electrode by induction, anode in the central compartment and cathode in the outer compartments.

On passing an electric current electrolysis of *NaCl* and *NaOH* takes place in outer and central compartments respectively. In the outer compartment Cl_2 is liberated at anode while sodium forms amalgam with mercury. This is brought into the central compartment by rocking motion given to the cell by eccentric wheel. In the central compartment, on the other hand, due to electrolysis of *NaOH*, OH^- ions are discharged at mercury anode where they combine with sodium amalgam to form sodium hydroxide. The Na^+ ions discharged at cathode react with water to form more of sodium hydroxide. The concentration of sodium hydroxide increases and is thus drawn off from time to time, evaporated and cast into sticks.



Castner Kellner Cell for Sodium hydroxide

Properties :

Physical : Sodium hydroxide is a white, crystalline solid. It is a *deliquescent* and usually marketted as sticks, flakes or pallets. It is highly soluble in water evolving much heat during dissolution. The solution is soapy to touch and is very corrosive. It melts at 318°C.

Chemical :

(1) It is a strong base. It changes colours of indicators e.g.

$$\text{Red litmus} \xrightarrow{NaOH} \text{Blue}$$

$$\text{Methyl orange}\xrightarrow{NaOH}\text{Yellow}$$

$$\text{Phenolphthalin}\xrightarrow{NaOH}\text{Pink}$$

(ii) **Action of air** : It absorbs CO_2 and forms sodium carbonate and with excess of CO_2 it forms a film of sodium bicarbonate.

(a) $2NaOH+CO_2 \rightarrow Na_2CO_3+H_2O$

(b) $Na_2CO_3+H_2O+CO_2 \rightarrow 2NaHCO_3$

(iii) **Action of acids** : It forms salts and water with acid :

(a) $NaOH+HCl \rightarrow NaCl+H_2O$

(b) $2NaOH+H_2SO_4 \rightarrow Na_2SO_4+2H_2O$

(iv) **Action with ammonium salts** : When any ammonium salt is treated with $NaOH$ solution then ammonia is evolved.

$$NH_4Cl+NaOH \rightarrow NaCl+NH_3+H_2O$$

(v) **Action with Metals** : Solution of caustic soda reacts with Zinc (Zn), Tin (Sn), Aluminium (Al), and Lead (Pb) forming salts and hydrogen.

$$Zn+2NaOH \rightarrow Na_2ZnO_2\ (\text{Sod. zincate})+H_2\uparrow$$

$$Sn+2NaOH+H_2O \rightarrow Na_2SnO_3\ (\text{Sod. stannate})+2H_2\uparrow$$

$$Pb+2NaOH \rightarrow Na_2PbO_2\ (\text{Sod. plumbite})+H_2\uparrow$$

$$2Al+2NaOH+2H_2O \rightarrow 2NaAlO_2\ (\text{Sod. aluminate})+3H_2\uparrow$$

(vi) **Action with non-metals** :

(a) Reaction with Boron and Silicon. It gives Hydrogen :

$$Si+2NaOH+H_2O \rightarrow Na_2SiO_3\ (\text{Sod. silicate})+2H_2\uparrow$$

(b) **Reaction with sulphur** : It reacts with sulphur forming a mixture of sodium thiosulphate and sodium pentasulphide.

$$6NaOH+4S \rightarrow 2Na_2S+Na_2S_2O_3+3H_2\uparrow$$

$$\underline{[\times 2]\ Na_2S+4S \rightarrow Na_2S_5\ (\text{Sod. poly sulphide})}$$

$$6NaOH+12S \rightarrow Na_2S_2O_3+3H_2+2Na_2S_5$$

(c) **Reaction with phosphorous** : It reacts with white or yellow phosphorus to give phosphine.

$$P_4+3NaOH+3H_2O \rightarrow PH_3\uparrow+3NaH_2PO_2$$

(d) **Reaction with chlorine** : The action of sodium hydroxide and chlorine can be classified as :

(i) Cold excess caustic soda (solution)

$$2NaOH+Cl_2 \rightarrow NaCl+NaOCl+H_2O$$

(ii) Hot solution of caustic soda :

$$2NaOH+Cl_2 \rightarrow NaCl+NaOCl+H_2O[\times 3]$$

$$\underline{3NaOCl \rightarrow NaClO_3+2NaCl}$$

$$6NaOH+3Cl_2 \rightarrow 5NaCl+NaClO_3+3H_2O$$

(iii) If chlorine is passed over molten caustic soda, oxygen is evolved.

$$4NaOH+2Cl_2\rightarrow 4NaCl+2H_2O+O_2$$

(vii) **Reaction with metallic salt solutions :** It reacts with solutions of metallic salts forming their hydroxides.

(a) $FeCl_3+3NaOH\rightarrow Fe(OH)_3\downarrow$ (Reddish brown) $+3NaCl$

(b) $CrCl_3+3NaOH\rightarrow Cr(OH)_3\downarrow$ (Green) $+3NaCl$

(c) (i) Little $NaOH$ solution and excess Zn salt then $Zn(OH)_2$ is obtained.

$$ZnSO_4+2NaOH\rightarrow Zn(OH)_2\downarrow+Na_2SO_4$$

(ii) Excess of $NaOH$ solution and little Zn salt then sodium zincate is obtained.

$$\begin{array}{c} ZnSO_4+2NaOH\rightarrow Zn(OH)_2\downarrow+Na_2SO_4\\ Zn(OH)_2+2NaOH\rightarrow Na_2ZnO_2+2H_2O\\ \hline ZnSO_4+4NaOH\rightarrow Na_2ZnO_2+Na_2SO_4+2H_2O \end{array}$$

(d) (i) Little $NaOH$ solution and excess of Al salts, then white gelatinous precipitate of $Al(OH)_3$ is obtained.

$$Al(NO_3)_3+3NaOH\rightarrow Al(OH)_3\downarrow+3NaNO_3$$

(ii) Excess of $NaOH$ solution and little Al salt then solution of sodium aluminate is obtained.

$$\begin{array}{c} Al(NO_3)_3+3NaOH\rightarrow Al(OH)_3\downarrow+3NaNO_3\\ Al(OH)_3+NaOH\rightarrow NaAlO_2+2H_2O\\ \hline Al(NO_3)_3+4NaOH\rightarrow NaAlO_2+3NaNO_3+2H_2O \end{array}$$

(viii) **Reaction with carbon monoxide :** When CO is passed under pressure into a solution of $NaOH$ at 100°C, then sodium formate is formed.

$$CO+NaOH\rightarrow HCOONa$$

(ix) **Reaction with organic compounds :** It reacts with chloroform ($CHCl_3$), Aldehydes (Formaldehyde—$HCHO$) and esters (ethyl acetate) as follows :

$$\underset{\text{Chloroform}}{CHCl_3}+4NaOH\longrightarrow \underset{\text{Sod. formate}}{HCOONa}+3NaCl+2H_2O$$

$$\underset{\text{Formaldehyde}}{2HCHO}+NaOH\xrightarrow{\text{heat}}\underset{\text{Methyl alcohol}}{CH_3OH}+\underset{\text{Sod. formate}}{HCOONa}$$

$$\underset{\text{Ethyl acetate}}{CH_3COO.C_2H_5}+NaOH\longrightarrow \underset{\text{Sod. acetate}}{CH_3COONa}+\underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

Uses :

1. In the manufacture of organic dye stuffs. 2. In refining petroleum and vegetable oils. 3. In the manufacture of soap, paper and artificial silk. 4. As a laboratory reagent. 5. In the purification of bauxite. 6. For mercerizing cotton. 7. For the manufacture of sodium, hypochlorites, chlorates etc.

4. Sodium carbonate, Washing soda, $Na_2CO_3.10H_2O$: Large deposits of crude sodium carbonate are found in certain areas like U.S.A., East Africa, India (U.P. and Bihar) etc. They consist mainly of the sesquicarbonate, commonly known as *trona*, $Na_2CO_3, NaHCO_3, H_2O$.

Manufacture : Sodium carbonate is manufactured by (1) The Lablanc process, (2) the electrolysis of caustic soda, (3) the ammonia-soda or Solvay process. Most of the washing soda is now manufactured by ammonia soda process.

(i) The Lablanc process : This method is now obsolete. The method involves three steps :

(a) The conversion of sodium chloride into sodium sulphate (called salt cake).

$$2NaCl+H_2SO_4\xrightarrow{\text{heat}}Na_2SO_4+2HCl$$

(b) The conversion of the salt cake into *black-ash* (a mixture of CaS and Na_2CO_3) by heating with lime stone and coke at a high temperature.

$$Na_2SO_4+CaCO_3+2C\rightarrow \underbrace{Na_2CO_3+CaS}_{\text{Black-ash}}+2CO_2$$

(c) Extraction of sodium carbonate from the black-ash by leaching it with water and purifying the product by crystallisation.

Defects of Lablanc process :

(i) This method requires big expenses due to use of H_2SO_4.

(ii) HCl vapour is evolved in the reaction which is harmful.

(iii) Sodium carbonate is not too much pure.

(ii) The Electrolytic process : In this process at first sodium hydroxide is obtained by the electrolysis of brine by the Kellner process. When CO_2 along with steam is passed through caustic soda solution under pressure, sodium carbonate is obtained.

$$NaCl \overset{\text{Electrolysis}}{\rightleftharpoons} Na^++Cl^-$$

Cathode $Na^++e\rightarrow Na$

$$2Na+H_2O\rightarrow 2NaOH+\tfrac{1}{2}H_2$$

$$2NaOH+CO_2\rightarrow Na_2CO_3+H_2O$$

Anode $Cl^-\rightleftharpoons\tfrac{1}{2}Cl_2+e$

(iii) Solvay's processes (*Commercial method*) :

Principle : It is based on the fact that when CO_2 is passed through saturated ammoniacal brine solution, $NaHCO_3$ is formed. It being slightly soluble in water gets precipitated.

$$NH_3+H_2O+CO_2\rightarrow NH_4HCO_3$$

$$NH_4HCO_3+NaCl\rightarrow NaHCO_3+NH_4Cl$$

The precipitate of bicarbonate is separated and strongly heated to get Sodium Carbonate

$$2NaHCO_3\rightarrow Na_2CO_3+H_2O+CO_2$$

Working : (i) Ammonia is allowed to bubble into saturated $NaCl$ solution in water called Ammonia absorber whereby the impurities of *Ca, Mg, Fe* etc. precipitate out as carbonates or hydroxide and a saturated ammoniacal brine solution is formed.

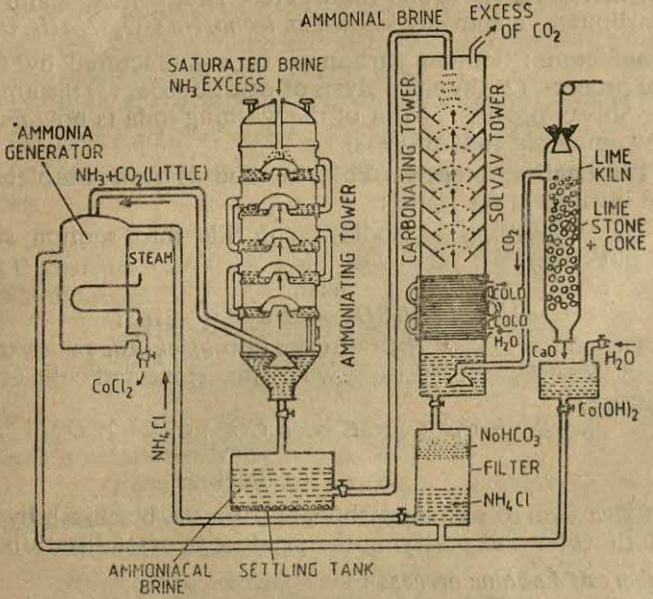


Fig. 64. Solvay Process

$$2NH_3+H_2O+CO_2 \rightarrow (NH_4)_2CO_3$$
$$CaCl_2+(NH_4)_2CO_3 \rightarrow CaCO_3\downarrow+2NH_4Cl$$
$$MgCl_2+2NH_4OH \rightarrow Mg(OH)_2\downarrow+2NH_4Cl$$

(ii) A clear ammoniacal brine solution is then allowed to drop into another tower called carbonating tower which is fitted up with perforated plates. A current of CO_2 is introduced under pressure from the bottom when sparingly soluble $NaHCO_3$ is formed.

(iii) The suspension of $NaHCO_3$ is taken out from the bottom of the carbonating tower and is filtered through *Rotatory vacuum* filters. The deposit of $NaHCO_3$ is separated from the filters and is ignited to get Na_2CO_3.

$$2NaHCO_3 \rightarrow Na_2CO_3+H_2O+CO_2$$

The CO_2 gas set free is utilised again.

(iv) The mother liquor, obtained by filtration, contains NH_4Cl., It is pumped to *Ammonia recovery tower* where it is heated with calcium hydroxide.

$$2NH_4Cl+Ca(OH)_2 \rightarrow CaCl_2+2NH_3+2H_2O$$

The ammonia evolved is used again.

Advantages : The process is in fact self-sufficient and moreover as the raw materials are cheap and the product obtained is of high purity, it is widely employed and preferred over Leblanc process.

Properties :

Physical : It is a white crystalline substance containing 10 molecules of water of crystallisation, $Na_2CO_3.10H_2O$. It is soluble in water. On exposive to air crystals effloresence to form monohydrate, $Na_2CO_3H_2O$. On heating to 750°C it becomes anhydrous and melts at 852°C.

Anhydrous sodium carbonate called soda ash is a white powder and absorbs moisture from the air forming monohydrate, $Na_2CO_3H_2O$.

Chemical :

(i) *Action of water* : It is soluble in water and hydrolyses to yield alkaline solution.

$$Na_2CO_3+2H_2O \rightleftharpoons \underset{\displaystyle 2Na^{+}+2OH^{-}}{\underset{\displaystyle \upharpoonleft\downharpoonright}{2NaOH}}+H_2CO_3$$

(ii) *Action of acids* : It reacts with acids to give salt, CO_2 and water.

$$Na_2CO_3+2HCl \rightarrow 2NaCl+CO_2+H_2O$$

(iii) *Action of* CO_2 : When CO_2 is passed into a cold concentrated solution of Na_2CO_3 then sodium bicarbonate is obtained.

$$Na_2CO_3+H_2O+CO_2 \rightleftharpoons 2NaHCO_3$$

(iv) *Action of Salts* : When Na_2CO_3 solution is added to solution of the salt then carbonates or basic carbonates of the metals are formed.

$$MCl_2+Na_2CO_3 \rightarrow MCO_3\downarrow+2NaCl\ (M=Ca^{+2}, Sr^{+2}, Ba^{+2})$$

$$2ZnSO_4+2Na_2CO_3+H_2O \rightarrow Zn(OH)_2.ZnCO_3+2Na_2SO_4+CO_2\uparrow$$

(v) *Action of Sulphur dioxide* : When SO_2 is passed into a solution of Na_2CO_3, a mixture of sodium sulphite and sodium bisulphite is formed.

$$Na_2CO_3+SO_2 \rightarrow Na_2SO_3+CO_2\uparrow$$

$$Na_2CO_3+2SO_2+H_2O \rightarrow 2NaHSO_3+CO_2\uparrow$$

Uses :

1. As washing soda for washing clothes. 2. As a laboratory reagent. 3. In the softening of water. 4. In the manufacture of glass, soap and caustic soda.

5. Conversion of Sodium Carbonate to Sodium Bicarbonate and vice versa :

(a) When CO_2 is passed into saturated solution of sodium carbonate then sodium bicarbonate is obtained.

$$Na_2CO_3+CO_2+H_2O \rightarrow 2NaHCO_3$$

(b) When sodium bicarbonate is heated then sodium carbonate is obtained.

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

Distinguish Between Sodium Bicarbonate and Sodium Carbonate :

Experiment	$NaHCO_3$	Na_2CO_3
1. Action of heat	CO_2 is evolved which turns lime water milky.	It becomes anhydrous. It melts but it does not give CO_2 on heating
2. Action of $CaCl_2$ solution	It does not give precipitate in cold.	It gives white precipitate of $CaCO_3$.
3. Action of CO_2 in the saturated solution of salt.	No change.	Sodium bicarbonate is precipitated.

6. Sodium Bicarbonate, $NaHCO_3$:

Preparation :

It is formed in large quantities as the intermediate product in the Solvay process. It may be obtained by passing CO_2 through a solution of sodium carbonate.

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$$

Properties : It is a white crystalline substance, sparingly soluble in water. Its solution turns methyl orange yellow but shows no change with phenolphthalein. It is very weak base but it is an acid salt. It decomposes at 100°C to give CO_2.

$$2NaHCO_3 \xrightarrow{100^\circ C} Na_2CO_3 + H_2O + CO_2\uparrow$$

Uses :

(i) In baking powder. (ii) In effervescent drinks e.g. sedlitz powders, fruit salts etc. (iii) In fire-extinguishers. (iv) In medicine for removing the acidity in the stomach.

7. Sodium Nitrate or Chili salt petre, $NaNO_3$:

It occurs in huge amounts as deposits in Chilli and Peru in South America. It can be obtained by the action of dil. HNO_3 on (a) $NaOH$ and (b) Na_2CO_3. The solution on crystallisation gives $NaNO_3$.

$$NaOH + HNO_3 \rightarrow NaNO_3 + H_2O$$
$$Na_2CO_3 + 2HNO_3 \rightarrow 2NaNO_3 + H_2O + CO_2\uparrow$$

Properties :

(i) It is a colourless, deliquescent, crystalline substance which is soluble in water.

(ii) It melts at 136° and decomposes on further heating to give $NaNO_2$ and O_2.

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2$$

For this reason C or S pieces if added in the melting sodium nitrate burn vigorously.

$$2NaNO_3 + S \rightarrow Na_2SO_4 + SO_2 + N_2$$
$$4NaNO_3 + C \rightarrow 2Na_2CO_3 + 3CO_2\uparrow + 2N_2$$

It reacts with sulphuric acid to form nitric acid.

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$

Uses :

(i) As an artificial manure in agriculture.

(ii) In the manufacture of HNO_3.

8. Sodium Nitrite, $NaNO_2$:

Preparation : It is prepared (i) by heating $NaNO_3$ to 400-500°C.

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2\uparrow$$

(ii) by heating $NaNO_3$ with Lead (Pb) at 400°C.

$$NaNO_3 + Pb \rightarrow NaNO_2 + PbO$$

(iii) *Manufacture* : When mixture of oxides of nitrogen is passed into sodium hydroxide or sodium carbonate solution then $NaNO_2$ is obtained.

$$2NaOH + NO + NO_2 \rightarrow 2NaNO_2 + H_2O$$
$$Na_2CO_3 + NO + NO_2 \rightarrow 2NaNO_2 + CO_2\uparrow$$

Properties :

(i) It is white crystalline compound when pure but usually slightly yellow. It is soluble in water.

(ii) *Action of acids* : It reacts with H_2SO_4 or HCl in cold to give nitrous acid (HNO_2) which decomposes to give nitric oxide gas.

$$NaNO_2 + H_2SO_4 \rightarrow NaHSO_4 + HNO_2$$
$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$

(iii) *Action of NH_4Cl* : When it is mixed with NH_4Cl and the mixture is heated then nitrogen (N_2) is evolved.

$$NaNO_2 + NH_4Cl \rightarrow NH_4NO_2 + NaCl$$
$$\underline{NH_4NO_2 \rightarrow N_2 + 2H_2O}$$
$$NaNO_2 + NH_4Cl \rightarrow N_2 + 2H_2O + NaCl$$

(iv) **As an oxidising agent :**

(a) *Reaction with acidified KI solution.* It reacts with acidified solution of KI to give I_2 and itself reduced to NO.

$$2NaNO_2 + H_2SO_4 \rightarrow NaHSO_4 + HNO_2\ [\times 2]$$
$$2HNO_2 \rightarrow 2NO + H_2O + 'O'$$
$$\underline{2KI + H_2SO_4 + 'O' \rightarrow K_2SO_4 + I_2 + H_2O}$$
$$2NaNO_2 + 3H_2SO_4 \rightarrow 2NaHSO_4 + 2NO + K_2SO_4 + 2H_2O$$

(b) *Reaction with acidified Ferrous salt* : When $NaNO_2$ is added to ferrous salt solution in presence of H_2SO_4 then ferric sulphate is obtained.

$$NaNO_2+H_2SO_4\rightarrow NaHSO_4+HNO_2[\times 2]$$
$$H_2S+2HNO_2\rightarrow S+2NO+2H_2O$$
$$\overline{2NaNO_2+2HCl+H_2S\rightarrow S+2NO+2H_2O+2NaCl}$$

(c) *Reaction with* H_2S :

H_2S in acid medium gives sulphur.

$$NaNO_2+HCl\rightarrow NaCl+HNO_2\,[\times 2]$$
$$H_2S+2HNO_2\rightarrow S+2NO+2H_2O$$
$$\overline{2NaNO_2+2HCl+H_2S\rightarrow S+2NO+2H_2O+2NaCl}$$

(v) As a reducing agent :

(a) *Reaction with acidified* $KMnO_4$ *solution*: When $NaNO_2$ is added to acidified $KMnO_4$ solution then the colour of $KMnO_4$ is decolourised.

$$2KMnO_4+3H_2SO_4\rightarrow K_2SO_4+2MnSO_4+3H_2O+5\text{'}O\text{'}$$
$$5NaNO_2+5\text{'}O\text{'}+5H_2SO_4\rightarrow 5HNO_3+5NaHSO_4$$
$$\overline{2KMnO_4+5NaNO_2+8H_2SO_4\rightarrow K_2SO_4+2MnSO_4+5HNO_3}$$
$$+3H_2O+5NaHSO_4$$

(b) *Reaction with acidified* $K_2Cr_2O_7$ *solution* : When $NaNO_2$ is added to acidified $K_2Cr_2O_7$ solution then colour of $K_2Cr_2O_7$ (orange) turns green. $[Cr_2(SO_4)_3]$.

$$K_2Cr_2O_7+4H_2SO_4\rightarrow Cr_2(SO_4)_3+K_2SO_4+4H_2O+3\text{'}O\text{'}$$
$$3NaNO_2+3\text{'}O\text{'}+3H_2SO_4\rightarrow 3NaHSO_4+3HNO_3$$
$$\overline{K_2Cr_2O_7+7H_2SO_4+3NaNO_2\rightarrow Cr_2(SO_4)_3+K_2SO_4+4H_2O}$$
$$+3NaHSO_4+3HNO_3$$

Uses : It is used in dye-industry and as reagent in the laboratory.

9. Sodium Sulphate (Glauber's salt), $Na_2SO_4.10H_2O$ **:**

Preparation : (i) It is prepared by heating $NaCl$ with conc. H_2SO_4.

$$2NaCl+H_2SO_4\rightarrow Na_2SO_4+2HCl$$

(ii) In the laboratory, the salt is prepared by the action of H_2SO_4 on caustic soda or sodium carbonate.

$$2NaOH+H_2SO_4\rightarrow Na_2SO_4+2H_2O$$
$$Na_2CO_3+H_2SO_4\rightarrow Na_2SO_4+CO_2+H_2O$$

It is formed as intermediate substance (salt cake) in the Leblanc process for the manufacture of sodium carbonate. The salt cake is dissolved in water and solution is crystallised by evaporation to obtain the *Glauber's salt.*

Properties :

(i) It is a colourless crystalline solid.
(ii) It is highly soluble in water.

(iii) It is an *efflorescent* substance and it loses water of crystallisation on exposure to air.

(iv) On heating with carbon it is reduced to sodium sulphide.

$$Na_2SO_4+4C\rightarrow Na_2S+4CO\uparrow$$

Uses :

(i) In the manufacture of glass and craft paper.
(ii) In the preparation of sodium thiosulphate.
(iii) In textile industries.
(iv) In medicine as purgative.

10. Sodium Thiosulphate (Hypo), $Na_2S_2O_3.5H_2O$:

Preparation :

(i) It is prepared by boiling sodium sulphite solution with flowers of sulphur and stirring the solution till the alkaline reaction disappears.

$$Na_2SO_3+S\rightarrow Na_2S_2O_3$$

The excess of sulphur is filtered off and the filtrate is evaporated when the crystals of sodium thiosulphate separate out.

(ii) By passing sulphur dioxide into sodium sulphide solution :

$$2Na_2S+3SO_2\rightarrow 2Na_2S_2O_3+S$$

(iii) **Spring's reaction** : By adding iodine to a mixture of sodium sulphite and sodium sulphide solutions.

$$Na_2S+Na_2SO_3+I_2\rightarrow 2NaI+Na_2S_2O_3$$

(iv) The pure hypo is best prepared by crystallising a solution of sodium hydrogen sulphide and sodium bisulphite.

$$2NaHS+4NaHSO_3\rightarrow 3Na_2S_2O_3+3H_2O$$

The hypo is purified by recrystallisation when it crystallises as

$$Na_2S_2O_3.5H_2O.$$

Properties :

(i) It is colourless crystalline substance.
(ii) It is soluble in water.

(iii) **Action of heat** : On heating it decomposes into sodium sulphate and penta sulphide.

$$4Na_2S_2O_3\rightarrow Na_2S_5+3Na_2SO_4$$

(iv) **Action of acids** : It decomposes on treatment with dilute mineral acids (Distinction from sulphites) e.g.

$$\begin{array}{c} Na_2S_2O_3+2HCl\rightarrow 2NaCl+H_2S_2O_3 \\ \underline{H_2S_2O_3\rightarrow H_2O+SO_2+S} \\ Na_2S_2O_3+2HCl\rightarrow 2NaCl+H_2O+SO_2+S \end{array}$$

or

$$S_2O_3^{-2}+2H^+\rightarrow H_2O+SO_2+S$$

(v) **Action of Silver halides** : Silver halides dissolve in sodium thiosulphate forming a complex anion e.g.

$$AgCl+2Na_2S_2O_3 \rightarrow \underset{\text{Sod. Argento thiosulphate}}{Na_3[Ag(S_2O_3)_2]} + NaCl$$

or $$Ag^+ + 2S_2O_3^{-2} \rightarrow [Ag(S_2O_3)_2]^{-3}.$$

(vi) **Action of Silver nitrate** : A silver nitrate solution on treatment with sodium thiosulphate solution gives a white precipitate of silver thiosulphate which is changed to black precipitate of silver sulphide.

$$Na_2S_2O_3+2AgNO_3 \rightarrow Ag_2S_2O_3\downarrow+2NaNO_3$$
$$Ag_2S_2O_3+H_2O \rightarrow \underset{\text{Black}}{Ag_2S\downarrow}+H_2SO_4$$

When sodium thiosulphate is used in excess a soluble complex salt, sodium argentothiosulphate is formed.

$$AgNO_3+2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2]+NaNO_3$$

(vii) **As a reducing agent** : Hypo behaves as a reducing agent.

$$2S_2O_3^{-2} \rightarrow S_4O_6^{-2}+2e$$

(a) **Reaction with Iodine** : Hypo solution decolourises iodine solution producing tetrathionate.

$$2Na_2S_2O_3+I_2 \rightarrow Na_2S_4O_6+2NaI$$
$$2S_2O_3^{-2}+I_2 \rightarrow S_4O_6^{-2}+2I^-$$

In this reaction iodine is reduced to iodide and thiosulphate is oxidised to tetrathionate. This reaction is used in volumetric analysis for iodometry titrations.

(b) **Reaction with Chlorine** : In this case chlorine is reduced into chloride ions by thiosulphate.

$$S_2O_3^{-2}+4Cl_2+5H_2O \rightarrow 2SO_4^{-2}+10H^++8Cl^{-1}$$

This reaction is used for removing excess chlorine from bleached fabrics.

(c) **Reaction with Ferric chloride** : It reduces ferric ions to ferrous ions.

$$2Fe^{3+}+2S_2O_3^{2-} \rightarrow 2Fe^{2+}+S_4O_6^{2-}$$

(d) **Reaction with Cupric salts** : It reduces cupric ions to cuprous ions.

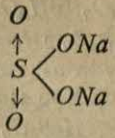
$$2Cu^{2+}+2S_2O_3^{2-} \rightarrow S_4O_6^{2-}+2Cu^+$$

(e) **Reaction with Auric salts** : It first reduces cupric ions into aurous ions which then form complexes.

$$AuCl_3+2S_2O_3^{2-} \rightarrow AuCl+S_4O_6^{2-}$$
$$AuCl+2S_2O_3^{2-} \rightarrow [Au(S_2O_3)_2]^{3-}+Cl^-$$

Uses : It is used (a) as a reducing agent, (b) in volumetric analysis in iodometric titrations, (c) in photography as a fixing agent, (d) as an antichlor to remove chlorine from bleached fabrics, (e) in medicine.

Structure :



11. Sodium Ammonium Hydrogen Phosphate, Microcosmic salt, $NaNH_4HPO_4.4H_2O$:

Preparation :

(i) It is prepared by crystallising di-sodium phosphate (Na_2HPO_4) and ammonium phosphate $(NH_4)_3 PO_4$ (5 : 2) together.

(ii) It is also prepared by dissolving ammonium chloride and disodium hydrogen phosphate in hot water.

$$Na_2HPO_4 + NH_4Cl \rightarrow Na(NH_4)HPO_4 + NaCl$$

It is purified by crystallisation.

Properties : When it is heated, it melts and forms a transparent mass which combines with metallic oxide to form coloured ortho-phosphates.

$$NaNH_4HPO_4 \rightarrow NaPO_3 \text{ (sod. metaphosphate)} + NH_3 + H_2O$$
$$NaPO_3 + CuO \rightarrow CuNaPO_4 \text{ (Blue)}$$

Uses : It is used in qualitative analysis and also for testing silica. The test is known as *Micro-cosmic bead test.*

12. Sodium tetraborate, Borax (Suhaga), $Na_2B_4O_7.10H_2O$

Tincal is a crude form of borax which contains about 55% borax. It is found in dried up lakes of Tibet, Ceylon, California.

Preparation : It is prepared by the following methods :

(i) From Tincal : Tincal is dissolved in water and the clear solution obtained by filteration is concentrated and crystallised when pure borax is obtained.

(ii) **From Colemanite** : It is a naturally occurring calcium borate. The mineral is boild with concentrated solution of sodium carbonate. The solution obtained on filteration is concentrated when crystals of borax are deposited.

$$\underset{\text{Colemanite}}{Ca_2B_6O_{11}} + 2Na_2CO_3 \rightarrow 3CaCO_3 \downarrow + \underset{\text{Borax}}{Na_2B_4O_7} + 2NaBO_2$$

A current of CO_2 is passed through the mother liquor to convert sodium metaborate to borax which is also crystallised out.

$$4NaBO_2 + CO_2 \rightarrow Na_2B_4O_7 + Na_2CO_3$$

The sodium carbonate so formed is used again for treating a fresh quantity of the mineral, colemanite.

Properties : It exists in three forms :

(a) Prismatic Borax—$Na_2B_4O_7.10H_2O$.

(b) Octahedral Borax—$Na_2B_4O_7.5H_2O$.

(c) Borax glass—It is anhydrous sodium tetraborate, $Na_2B_4O_7$. It is soluble in water and the solution is alkaline in nature.

$$Na_2B_4O_7+2H_2O \rightleftharpoons \underset{\text{weak acid}}{H_2B_4O_7} + \underset{\text{strong base}}{2NaOH}$$

Action of Heat : On heating borax loses water of crystallisation and swells up to a white opaque mass. The anhydrous mass fuses at 740°C forming borax glass which combines with metallic oxide forming coloured metaborate, the colour depending upon the metallic oxides. This serves as a test for some metals and is known as Borax bead test. For example—

$$Na_2B_4O_7 \rightarrow 2NaBO_2+B_2O_3$$
$$B_2O_3+CoO \rightarrow Co(BO_2)_2 \text{ (intense blue)}$$
$$B_2O_3+CuO \rightarrow Cu(BO_2)_2 \text{ (light blue)}$$

Uses : (i) In borax bead test in the qualitative analysis.

(ii) In leather industry for clearing hides and skins and in leather dyeing.

(iii) In the manufacture of enamels, glasses, for pottery and tiles.

(iv) As a flux in soldering welding and in the extraction of metals.

(v) In pyrex glass.

(vi) For impregnating match sticks to prevent after glow.

13.4. Potassium

Symbol—K, At. No. 19, At. wt. 39.1
Electronic configuration : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

History : It was isolated by Davy in 1808 by the electrolysis of caustic potash.

Occurrence : Potassium is somewhat more reactive than sodium and does not occur free in nature. The important minerals of potassium are as follows :

(i) *Chlorides* : Carnallite—$KCl.MgCl_2.6H_2O$,
Sylvine KCl.

(ii) *Nitrate* : Nitre or saltpetre, KNO_3.

(iii) *Silicate* : Felspar—$KAlSi_3O_2$, Mica—$KH_2Al_3(SiO_4)_3$.

All land plants contain potassium compounds which they derive from soil.

Extraction : It is extracted by any of the following methods :

1. By the electrolysis of the fused potassium hydroxide.

2. By heating potassium carbonate with charcoal.

$$K_2CO_3+2C \rightarrow 2K+3CO\uparrow$$

3. The metal is best obtained by the electrolysis of fused potassium chloride (Down process).

$$KCl \rightarrow K^+ + Cl^-$$

Cathode $K^+ + e \rightarrow K$

Anode $2Cl^- \rightarrow Cl_2 + 2e$

4. By the electrolysis of fused KCN.

5. It can also be obtained by heating KF with CaC_2.

$$K_2F_2 + CaC_2 \rightarrow 2K + CaF_2 + 2C$$

Properties :

Physical : It is a silvery white soft metal and can be cut with a knife. It melts at 63°C and boils at 762°C. It is lighter than sodium.

Chemical : It closely resembles potassium. It is more reactive than sodium. It forms superoxide, KO_2, when reacted with excess of oxygen.

Uses : It is used in photoelectric cell.

2. In the synthesis of organic compound.

13 5. Compounds of Potassium

1. Potassium Superoxide, KO_2 :

When potassium is burnt in excess of oxygen then potassium superoxide, KO_2, is obtained. It is yellow solid, soluble in water.

It is a powerful oxidising agent.

2. Potassium Hydroxide, KOH (caustic potash) :

Preparation : It can be prepared

(i) by the electrolysis of potassium chloride solution.

(ii) by the action of lime on potassium carbonate.

$$K_2CO_3 + Ca(OH)_2 \rightarrow 2KOH + CaCO_3\downarrow$$

(iii) by the action of barium hydroxide on potassium sulphate.

$$K_2SO_4 + Ba(OH)_2 \rightarrow BaSO_4\downarrow + 2KOH$$

Properties :

(i) It is a white, highly deliquescent substance.

(ii) It closely resembles $NaOH$ in properties but is more soluble in water and particularly in alcohol.

(iii) It is stronger alkali than sodium hydroxide.

Uses :

(i) In the manufacture of soft soap.

(ii) As a reagent in organic chemistry.

(iii) As a absorbent for CO_2 and SO_2.

Properties : It exists in three forms :

(a) Prismatic Borax—$Na_2B_4O_7.10H_2O$.

(b) Octahedral Borax—$Na_2B_4O_7.5H_2O$.

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$$\underset{}{Na_2B_4O_7+2H_2O} \rightleftharpoons \underset{\text{weak acid}}{H_2B_4O_7} + \underset{\text{strong base}}{2NaOH}$$

Action of Heat : On heating borax loses water of crystallisation and swells up to a white opaque mass. The anhydrous mass fuses at 740°C forming borax glass which combines with metallic oxide forming coloured metaborate, the colour depending upon the metallic oxides. This serves as a test for some metals and is known as Borax bead test. For example—

$$Na_2B_4O_7 \rightarrow 2NaBO_2+B_2O_3$$
$$B_2O_3+CoO \rightarrow Co(BO_2)_2 \text{ (intense blue)}$$
$$B_2O_3+CuO \rightarrow Cu(BO_2)_2 \text{ (light blue)}$$

Uses : (i) In borax bead test in the qualitative analysis.

(ii) In leather industry for clearing hides and skins and in leather dyeing.

(iii) In the manufacture of enamels, glasses, for pottery and tiles.

(iv) As a flux in soldering welding and in the extraction of metals.

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Occurrence : Potassium is somewhat more reactive than sodium and does not occur free in nature. The important minerals of potassium are as follows :

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Properties :

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Properties :

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(ii) It closely resembles $NaOH$ in properties but is more soluble in water and particularly in alcohol.

(iii) It is stronger alkali than sodium hydroxide.

Uses :

(i) In the manufacture of soft soap.

(ii) As a reagent in organic chemistry.

(iii) As a absorbent for CO_2 and SO_2.

3. Potassium Iodide, KI :

It can be prepared by methods used for potassium bromide.

Manufacture : A mixture of iron filings, iodine and water with a concentrated solution of K_2CO_3.

$$3Fe+4I_2 \rightarrow Fe_3I_8$$

$$Fe_3I_8+4K_2CO_3+4H_2O \rightarrow 2Fe(OH)_3\downarrow+Fe(OH)_2\downarrow+8KI+4CO_2$$

The iron hydroxide are filtered off and potassium iodide is crystallised out from the solution.

Properties : (i) It is a white, crystalline solid, very soluble in water and alcohol.

(ii) Chlorine displaces iodine from its solution.

$$2KI+Cl_2 \rightarrow 2KCl+I_2$$

(iii) H_2SO_4 or HNO_3 decomposes it to iodine.

$$KI+H_2SO_4 \rightarrow KHSO_4+HI\ [\times 2]$$

$$\underline{2HI+H_2SO_4 \rightarrow 2H_2O+SO_2+I_2}$$

$$2KI+3H_2SO_4 \rightarrow 2KHSO_4+2H_2O+SO_2+I_2$$

(iv) Potassium iodide when added to $CuSO_4$ solution gives a white precipitate of cuprous iodide which appears brown due to the liberation of iodine.

$$2CuSO_4+4KI \rightarrow \underset{\text{(unstable)}}{2CuI_2}+2K_2SO_4$$

$$2CuI_2 \rightarrow Cu_2I_2+I_2$$

(v) When KI is added to a solution of mercuric chloride a scarlet precipitate of mercuric iodide is obtained which is soluble in excess of KI.

$$HgCl_2+2KI \rightarrow HgI_2+2KCl$$

$$HgI_2+2KI \rightarrow K_2[HgI_4]$$

An alkaline solution of potassium mercuric iodide, K_2HgI_4, is known as Nessler's reagent which is used in the detection of ammonia.

(vi) Potassium iodide solution is a good solvent for iodine.

$$KI+I_2 \rightleftharpoons KI_3$$

Uses : It is used in medicines (throat paints, tincture of iodine, in photography), as solvent for iodine and as a laboratory reagent.

4. Potassium Chlorate, $KCLO_3$:

It can be prepared by the following methods :

(i) By passing chlorine into boiling solution of caustic potash.

$$6KOH+3Cl_2 \rightarrow KClO_3+5KCl+3H_2O$$

Potassium chlorate being less soluble is separated by fractional crystallisation.

(ii) It is manufactured by passing chlorine in hot milk of lime.

$$6Ca(OH)_2+6Cl_2 \rightarrow Ca(ClO_3)_2+5CaCl_2+6H_2O$$

The unreacted lime is allowed to settle and to the filtered solution calculated quantity of potassium chloride is added when potassium chlorate is formed.

$$Ca(ClO_3)_2 + 2KCl \rightarrow 2KClO_3 + CaCl_2$$

Potassium chlorate being less soluble than calcium chloride separates out. It is further purified by crystallisation.

(iii) Modern Electrolytic Process : An aqueous solution of potassium chloride at 68°-70°C containing little HCl and $K_2Cr_2O_7$ is electrolysed in a cell provided with a number of electrodes very close to each other.

$$\begin{gathered} KCl \rightleftharpoons K^+ + Cl^- \\ K^+ + e \rightarrow K;\ 2Cl^- \rightarrow Cl_2 + 2e \\ 2K + 2H_2O \rightarrow 2KOH + H_2\ [\times 3] \\ \underline{6KOH + 3Cl_2 \rightarrow KClO_3 + 5KCl + 3H_2O} \\ \overline{6KCl + 3H_2O \rightarrow KClO_3 + 5KCl + 3H_2O} \end{gathered}$$

(Potassium dichromate improves the current efficiency and prevents the reduction of chlorate by hydrogen evolved at the cathode.)

Properties : (i) It is a white crystalline substance with a glassy appearance. It is sparingly soluble in cold water but more so in hot water. Its specific gravity is 2·65 and melting point 370°C.

(ii) On heating it gives oxygen. The reaction takes place as follows :

$$4KClO_3 \xrightarrow{380^\circ C} 3KClO_4 + KCl$$

$$KClO_4 \xrightarrow{650^\circ C} KCl + 2O_2$$

The decomposition is catalysed by manganese dioxide whereby the decomposition occurs at a considerable low temperature (200-400°C)

This reaction is employed for the laboratory preparation of oxygen.

(iii) When heated with hydrochloric acid potassium chlorate decomposes with the liberation of mixture of chlorine dioxide, known as euchlorine (yellow coloured gas).

$$2KClO_3 + 4HCl \rightarrow 2KCl + \underbrace{Cl_2 + 2ClO_2}_{\text{eu-chlorine}} + 2H_2O$$

(iv) With conc. sulphuric acid, chlorine dioxide is evolved with explosion.

$$3KClO_3 + 3H_2SO_4 \rightarrow 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O$$

(v) When potassium chlorate solution is heated with iodine and nitric acid, potassium iodine is formed.

$$2KClO_3 + I_2 \rightarrow 2KIO_3 + Cl_2$$

Uses : 1. Potassium chlorate is a powerful oxidising agent and is used in the manufacture of matches, fire works, gun powder and photographic flash powders.

2. It is used in the laboratory as an oxidising agent and as a source of oxygen.

3. It is antiseptic and its dilute solution is used in gargling :

5. Potassium Nitrate, Nitre, Salt Petre, KNO_3 :

It is commonly known as Shora and occurs in India and Ceylon.

Preparation : It is obtained on large scale from potassium chloride and sodium nitrate by double decomposition.

$$KCl+NaNO_3 \rightarrow KNO_3+NaCl$$

On evaporation, less soluble sodium chloride separates out and is filtered off. On cooling the filtrate, potassium nitrate crystallises out.

Properties : (i) It is a white crystalline, solid soluble in water. It resembles sodium nitrate in all its reactions excepting that it is not hygroscopic.

(ii) It melts at 336°C and on further heating evolves oxygen.

$$2KNO_3 \rightarrow 2KNO_2+O_2$$

Hence the fused potassium nitrate is a powerful oxidising agent.

(iii) A piece of sulphur or charcoal burns vigorously when thrown in molten potassium nitrate.

$$4KNO_3+5C \rightarrow 2K_2CO_3+3CO_2+2N_2$$
$$2KNO_3+2S \rightarrow K_2SO_4+SO_2+N_2$$

(iv) It forms nitric acid when heated with conc. sulphuric acid.

$$KNO_3+H_2SO_4 \rightarrow KHSO_4+HNO_3$$

Uses : (i) As a laboratory reagent and in medicine.

(ii) As a fertilizer.

(iii) In making meat and in refrigeration.

(iv) In packing fire-works and gun powder.

Gun powder is a mixture of nitre (six parts), charcoal (one part) and sulphur (one part).

6. Potassium Carbonate, Potash (Pearl Ash), K_2CO_3 :

Preparation : 1. It was formerly made by extracting wood ashes which contains about 15% K_2CO_3. The ashes are extracted with water and the clear solution is evaporated to dryness.

2. It can be formed by Leblanc process using KCl in place of $NaCl$. The Solvay process cannot be used, as potassium bicarbonate is highly soluble in water and does not precipitate like sodium bicarbonate.

3. On large scale it is now manufactured by passing carbon dioxide into a concentrated solution of potassium chloride containing solid hydrated magnesium carbonate at 20°C when potassium hydrogen magnesium carbonate is precipitated.

$$2KCl+2(MgCO_3.3H_2O)+CO_2 \rightarrow 2(MgCO_3.KHCO_3+MgCl_2.6H_2O)$$

The precipitate is separated by filtration and then decomposed by heating with water.

$$2(MgCO_3 \cdot KHCO_3 \cdot 4H_2O) \rightarrow 2MgCO_3 + K_2CO_3 + 9H_2O + CO_2$$

4. Pure potassium carbonate can be prepared by heating pure potassium bicarbonate or potassium hydrogen tartarate.

$$2KHCO_3 \rightarrow K_2CO_3 + H_2O + CO_2$$
$$2KHC_4H_4O_6 \rightarrow K_2CO_3 + 3C + 5H_2O + 4CO$$

Properties : It is a white deliquescent solid, very soluble in water. Its solution absorbs carbon dioxide forming potassium bicarbonate.

$$K_2CO_3 + H_2O + CO_2 \rightleftharpoons 2KHCO_3$$

The bicarbonate on heating gives pure potassium carbonate. It resembles Na_2CO_3 chemical properties. On heating it in steam it gives carbon dioxide.

$$K_2CO_3 + H_2O \rightarrow 2KOH + CO_2$$

Uses : (i) In the manufacture of soft soap and hard glass.

(ii) As a drying agent in the laboratory.

(iii) In preparing fusion mixture, which is a mixture of K_2CO_3 and Na_2CO_3.

6. **Fusion Mixture** : It is an equimolecular mixture containing Na_2CO_3 and K_2CO_3. The melting point of the mixture is less than the melting point of each individual. It is used in salt test.

Analytical Tests for Potassium

(i) Flame Test : Potassium salts impart characteristic violet colour to the bunsen flame. The flame appears pure when through blue cobalt glasses.

(ii) When a conc. solution of tartaric acid is added to a solution of potassium salt followed by a little alcohol, a white crystalline precipitate of potassium hydrogen tartarate is obtained.

(iii) On adding a solution of sodium cobalt nitrite to a solution of potassium salt, a yellow precipitate of potassium cobaltinitrite, $K_3[Co(NO_2)_6]$, is obtained.

(iv) With picric acid a yellow precipitate of potassium picrate is obtained.

TYPICAL QUESTIONS WITH ANSWER

1. How will you test if a specimen of caustic soda is free from chloride and carbonate ?

Solution : *Test for chloride* : Caustic soda solution is acidified by HNO_3 and $AgNO_3$ solution is added to it. If white precipitate is obtained, then caustic soda contains chloride as impurity.

$$NaCl + AgNO_3 \rightarrow AgCl\downarrow + NaNO_3$$

Test for Carbonate : Caustic soda is treated with dil. HCl then a gas with effervescence is evolved. The gas turns lime water milky and no effect on acidified solution. Hence caustic soda contains carbonate as impurity.

2. How will you bring about the following conversion ?

(a) Sodium to (i) sodium hydroxide, (ii) sodium carbonate, (iii) sodium peroxide.

(b) Sodium carbonate to sodium bi-carbonate and vice versa.

(c) $NaCl$ to (i) $NaOH$, (ii) Na_2CO_3, (iii) $NaHCO_3$.

Solution : *Sodium to Sodium hydroxide* : (a) (i) When a piece of sodium is dropped in water then sodium hydroxide solution is obtained. The solution is evaporated, then solid sodium hydroxide is obtained.

$$2Na+2H_2O \rightarrow 2NaOH$$

(ii) *Sodium to Sodium carbonate* : $NaOH$ from sodium is prepared as in (i) then CO_2 is passed into the solution of $NaOH$. $NaHCO_3$ is obtained. Which on heating gives Na_2CO_3.

$$NaOH+CO_2 \rightarrow NaHCO_3$$
$$2NaHCO_3 \rightarrow Na_2CO_3+H_2O+CO_2$$

(iii) *Sodium to Sodium peroxide* : When sodium is burnt in oxygen then sodium peroxide is obtained,

$$2Na+O_2 \rightarrow Na_2O_2$$

(b) Na_2CO_3 to $NaHCO_3$ and vice versa. See page 409-410

(c) (i) $NaCl$ to $NaOH$—Electrolytic process

(ii) $NaCl$ to Na_2CO_3—Solvay process

(iii) $NaCl$ to $NaHCO_3$—Prepare $NaCl$ to Na_2CO_3 by Solvay Process.

Then pass CO_2 into the solution of Na_2CO_3
Which on heating gives $NaHCO_3$.

$$Na_2CO_3+CO_2+H_2O \rightarrow 2NaHCO_3$$

3. Make a list of sodium salts which evolve gas :

(a) with dilute H_2SO_4, (b) with strong H_2SO_4.

Write the formulae of the gases, and indicate how you would test each with a view to ascertain the nature of the original salt.

Solution :

(a) Solutions which give gases with dil. H_2SO_4 :

Salts	*Formula of Gas*	*Test of the Gas*
(i) Na_2CO_3 $NaHCO_3$	CO_2 CO_2	The gas turns lime water milky.
(ii) Na_2S	H_2S	The gas turns lead acetate paper black.
(iii) Na_2SO_3	SO_2	The gas turns acidified $K_2Cr_2O_7$ solution green.
(iv) $NaNO_2$	$NO+NO_2$ (Brown)	The gas turns ferrous sulphate solution brown.

(b) Sodium salts which give gases with conc. H_2SO_4 :

Salts	*Formula of Gas*	*Test of the Gas*
(i) $NaCl$	HCl	It gives white fumes with ammonia.
(ii) $NaBr$	Br_2	Brown gas. It gives brown solution with CS_2.
(iii) NaI	I_2	Violet gas. It gives violet solution with CS_2.
(iv) $NaNO_3$	HNO_3 vapour	The test tube containing salt and conc. H_2SO_4 is mixed with Cu turnings then reddish brown gas is evolved.

4. Pure sodium chloride is not deliquescent, but the ordinary common salt is deliquescent, why ?

Solution : Pure sodium chloride is not deliquescent, but the ordinary common salt contains small amounts of magnesium chloride as impurities, which is deliquescent. Ordinary common salt is deliquescent due to the presence of magnesium chloride.

5. Explain the following :

(a) Aqueous solution of Na_2CO_3 is alkaline.

(b) Aqueous solution of Borax is alkaline.

(c) Aqueous solution of $NaCl$ is neutral.

(d) Aqueous solution of NH_4Cl is acidic.

Solution :

(a) In aqueous solution :

$$\underset{}{Na_2CO_3+H_2O} \rightleftharpoons \underset{\text{strong base}}{2NaOH} + \underset{\text{weak acid}}{H_2CO_3}$$

Since the base is strong hence the resulting solution is basic or alkaline.

(b) In aqueous solution :

$$Na_2B_4O_7+2H_2O \rightleftharpoons \underset{\text{weak acid}}{H_2B_4O_7} + \underset{\text{strong base}}{2NaOH}$$

Since the base is strong and acid is weak, hence the resulting solution is alkaline.

(c) Since $NaCl$ is not hydrolysed by water, hence the solution is neutral.

(d) In aqueous solution :

$$NH_4Cl+H_2O \rightleftharpoons \underset{\text{weak alkali}}{NH_4OH} + \underset{\text{strong acid}}{HCl}$$

Since the acid is strong hence the resulting solution is acidic.

6. How would you distinguish between

(a) $NaCl$ and KCl, (b) $NaNO_3$ and $NaNO_2$,
(c) Na_2SO_4 and Na_2SO_3 (d) KBr and KNO_3
(e) Na_2S and Na_2SO_3 ?

Solution : (a) $NaCl$ imparts golden yellow colour in flame test whereas KCl imparts a violet colour to the bunsen flame.

(b) When dil. mineral acids are added to $NaNO_2$ then brown fumes (due to NO and NO_2) are evolved whereas $NaNO_3$ does not give brown fumes with dil. acids.

$$2NaNO_2+2HCl \rightarrow 2NaCl+H_2O+NO+NO_2$$

$$NaNO_3+HCl \rightarrow \text{no reaction.}$$

(c) When barium chloride solution is added to the acidified solution of Na_2SO_4 (acidified with HCl or HNO_3) then white precipitate is obtained. But Na_2SO_3 does not give white precipitate with barium chloride solution in acid medium.

(d) On treatment with silver nitrate solution, KBr gives light yellow precipitate of $AgBr$ which is insoluble in dilute HNO_3.

$$KBr+AgNO_3 \rightarrow AgBr\downarrow+KNO_3$$

KNO_3 does not give this test. It however gives ring test.

(e) When dil. HCl is added to the salt, then a gas with rotten egg's smell is evolved which turns lead acetate paper black. Hence the salt is Na_2S.

$$Na_2S+2HCl \rightarrow 2NaCl+H_2S$$

Na_2SO_3 also gives gas with HCl but it does not turn lead acetate paper black.

QUESTIONS

Long Type Questions :

1. Comment on the position of sodium and potassium in the peroxide table.
2. Present a comparative study of group IA elements from the view point of periodic table.
3. Name the principal ores of sodium. How is sodium manufactured from sea salt ? What is the by-product of this process ? Why is sodium kept under kerosine oil ?
   What happens when (a) a piece of sodium is put in moist air, (b) a piece of sodium is put into water, (c) a piece of sodium is dipped into mercury ? Give equations where necessary. **(B. U. 1976 A; Bhag. U. '67 A; R. U. '68 A; '78 S; M. U. '68 A; P. U. '69 A)**
4. When a piece of sodium is placed in water, it diminishes in size, gradually and finally disappears. In what ways is the disappearance of sodium different from the ordinary process of solution in water ?
   How could metallic sodium be recovered from the liquid ?
5. Explain the manufacture of any two industrially important products from common salt.
6. How is the electrolysis of brine carried out on a large scale ? What products are obtained by this method ? **(P. U. 1970 A; Bhag. U. '69 A; M. U. '70 A; R. U. '73 A, '75 S)**
7. How does a solution of caustic soda react with—
   (a) nitrogen peroxide **(Bhag. U. 1963 S; R. U. '70 A)**, (b) zinc dust or zinc **(P. U. '73 A; Bhag. U. '69 A)**, (c) a solution of mercuric nitrate **(P. U. '57 A)**, (d) phosphorus **(P. U. '70 A; R. U. '78 A)**, (e) an aqueous solution of mercuric chloride **(P. U. '69 A)**, (f) ammonium chloride **(R. U. '78 A)**, (g) zinc sulphate **(R. U. '78 A)**, (h) mercurous nitrate, (i) air, (j) chlorine **(P. U. '70 A; B. U. '71 A; R. U. '75 S; Bhag. U. '69 A)**, (k) carbon dioxide **(P. U. '70 A: B. U. '71 A; R. U. '74 A)**, (l) Copper sulphate **(R. U. '74 A, '78 A; P. U. '64 A; B. U. '67 S)**, (m) ammonium sulphate **(B. U. '67 S)**, (n) sulphur dioxide **(R. U. '78 A, B. U. '70 A)**, (o) alumininm **(R. U. '70 A)**, (p) iodine, (q) carbon monoxide **(R. U. '70 A)** ?
8. Compare the reactions of caustic soda and ammonium hydroxide with the following substances, especially noting the colour changes and formation of precipitates.
   (a) Copper sulphate, (b) Ferric chloride, (c) Mercuric chloride, (d) Zinc sulphate, (e) Mercurous nitrate. **(B. U. 1956 A; P. U. '74 A, '75 S)**
9. How would you test if a specimen of caustic soda is free from chloride and carbonate ?
   What are the important uses of caustic soda ?
   (M. U. 1965 A; R. U. '73 A, '75 S; B. U. '67 S)
10. Describe the Leblanc's Process for the manufacture of sodium carbonate. What is the cause to replace this method by Solvay process ? **(B. U. 1966 S)**
    Write down in short the properties of sodium carbonate. **(P. U. 1964 A)**

11. How will you distinguish between—
    (a) sodium carbonate and sodium bicarbonate,
    (b) soda and caustic soda ?

12. Describe in detail a method for converting sodium chloride to sodium carbonate. **(P. U. 1966 S, '78 A; M. U. '68 A; Bhag. U. '76 A; R. U. '76 A; B. I. E. C. '83).**

13. How is sodium carbonate converted into bicarbonate and vice versa ? **(B. U. 1963 A; B. I. E. C. '83).** State the important uses of sodium carbonate.

14. Write chemical formula of each of the following :
    (a) Hypo (b) Washing soda (c) Caustic soda (d) Baking soda (e) Borax (f) Nitre (g) Chile salt petre (h) Glauber salt (i) Soda glass (j) Potash alum. **(IIT Gr. B. 1969)**

15. How will you distinguish between :
    (a) KNO_3 and KBr
    (b) Na_2CO_3 and Na_2SO_3
    (c) $NaNO_3$ and $NaNO_2$
    (d) $NaCl$ and KCl
    (e) K_2SO_4 and K_2SO_3
    (f) $NaCl$ and NH_4Cl ? **(IIT 1970, '71)**

16. Write the equation for the conversion of :
    (a) $NaCl$ to $NaOH$
    (b) Na_2CO_3 to $NaCl$
    (c) Na from $NaCl$
    (d) $NaCl$ from Na_2SO_4. **(IIT 1963, '70)**

17. What happens when :
    (a) Na reacts with water ? **(IIT 1977)**
    (b) a solution of $NaCl$ is electrolysed with inert electrodes ? **(IIT 1977)**
    (c) sodium treated with excess of air and the product is treated with cold dil. H_2SO_4. ? **(IIT 1968)**
    (d) $NaOH$ reacts with Zn and Al separately ? **(IIT 1974 A)**

18. How is potassium extracted from carnallite ore ? How KCl is converted into potassium carbonate ?

19. Why potassium carbonate be not prepared by a process similar to Solvay process for the manufacture of sodium carbonate ? What is fusion mixture ?

SHORT QUESTION

20. What happens when caustic soda reacts with :
    (a) zinc (b) ammonium chloride (c) chlorine (d) copper sulphate ?

21. Fill up the blanks and balance :
    (a) $Na_2CO_3+HCl\rightarrow$
    (b) $NaHCO_3\xrightarrow{\text{heated}}$
    (c) $P_4+NaOH+\qquad\qquad\rightarrow PH_3+NaH_2PO_2$
    (d) $NaOH+CO_2\rightarrow$
    (e) $ZnSO_4+NaOH\rightarrow Na_2ZnO_2+\cdots\cdots+\cdots\cdots$
    (f) $KOH+Cl_2\xrightarrow{\text{hot}}KCl+\cdots\cdots+\cdots\cdots$

22. Write notes on :
    (a) Fusion mixture (b) Castner Kellner process (c) Glauber's salt (d) Borax (e) Hypo (f) Washing soda (g) Nitre (h) Potash alum. **(BIEC 1984]**

23. Match A with B.

A	*B*
1. Glauber's salt	(a) $NaOH$
2. Hypo	(b) $Na_2B_4O_7.10H_2O$
3. Fusion mixture	(c) $NaHCO_3$
4. Caustic soda	(d) $Na_2SO_4.10H_2O$
5. Microcosmic salt	(e) Na_2SiO_3
6. Borax	(f) $NaNH_4HPO_4$
7. Baking soda	(g) $Na_2CO_3.K_2CO_3$
8. Water glass	(h) $Na_2S_2O_3.5H_2O$

24. You are given the names of the processes in *A* and substance in *B*. **Match A and B.**

A	*B*
1. Leblanc process	(a) $NaOH$
2. Solvay process	(b) Na_2CO_3
3. Nelson process	(c) Na
4. Down process	

25. Explain the following :

(a) Why sodium is not kept in water ?

(b) Why sodium is not obtained by the electrolysis of aqueous solution of $NaCl$?

(c) Why K_2CO_3 is not prepared by process similar to Solvay process ?

(d) In the manufacture of sodium by Down process, $CaCl_2$ is added to sodium chloride.

(e) An aqueous solution of iodine becomes colourless on adding $NaOH$ solution.

(f) Sodium metal is prepared by the electrolysis of fused $NaCl$ and not by the electrolysis of aqueous $NaCl$ solution.

26. How would you distinguish between

(a) KNO_2 and $NaNO_2$ (b) K_2SO_4 and Na_2SO_4

(c) KNO_3 and KNO_2 (d) KCl and $NaCl$

(e) K_2CO_3 and K_2SO_3 (f) Na_2S and Na_2SO_4 ?

27. How would you bring about the following conversion :
(a) $NaCl$ to (i) $NaOH$ (ii) Na_2CO_3 (iii) $NaHCO_3$?
(b) $NaCl$ to (i) Na (ii) $NaOH$?
(c) Na to (i) $NaOH$ (ii) $NaCl$ (iii) Na_2CO_3 (iv) $NaHCO_3$?

28. Identify A, B, C, D etc. in the following :

(i)
$$\begin{tikzcd}
\text{Fused } NaCl \arrow[r, "\text{Electrolysis}"] & \underset{\text{Cathode}}{A} \arrow[d, "\substack{H_2O \\ CO_2}"] & + & \underset{\text{Anode}}{B} \\
& C \arrow[r] & D &
\end{tikzcd}$$

(ii)
$$\begin{tikzcd}
\text{Aqueous } NaOH \arrow[r, "CO_2"] & A \arrow[r, "CO_2", "\text{excess}"'] & B \arrow[r, "\text{heat}"] & C \arrow[d, "HCl"] \\
& & & D\ (\text{gas})
\end{tikzcd}$$

Select and write the correct answer for the following :

29. Which of the following substance gives a flame colouration different from the other ?
1. Table salt 2. Borax 3. Caustic Potash 4. Washing soda.

30. Which of the following gives H_2 when boiled with $NaOH$?
1. Mg 2. Fe 3. Zn 4. Cu.

31. Which of the following does not decompose on heating ?
1. $NaHCO_3$ 2. $KHCO_3$ 3. $NaNO_3$ 4. Na_2CO_3.

32. Which of the following process is used for the manufacture of caustic soda ?
1. Nelson process 2. Solvay process
3. Down process 4. Lablanc's process.

33. The most abundant are of sodium is
1. Sodium carbonate 2. Sodium chloride
3. Sodium sulphate 4. Sodium phosphate.

34. Which of the following is called Glauber's salt ?
1. $Na_2CO_3.10H_2O$ 2. $Na_2S_2O_3.5H_2O$
3. $Na_2B_4O_7.10H_2O$ 4. $Na_2SO_4.10H_2O$.

35. Which of the following statement about the alkali metals is wrong ?
1. They have one electron in the outermost orbit.
2. They have one electron more than preceding inert gases.
3. They are s-block elements.
4. They have one electron less than preceding inert gases.

36. It would be dangerous to drop a piece of sodium into :
1. Paraffin 2. Petrol 3. Mineral oil 4. Dilute $NaCl$ solution.

37. Which of the following is most electropositive ?
1. H 2. Li 3. Na 4. K. **(PMDT 1978)**

38. Which of the following salt solution will give no precipitate when $NaOH$ solution is added to them ?
1. $CuSO_4$ 2. $ZnSO_4$ 3. $FeCl_3$ 4. $MgCl_2$.

39. Metal soluble in $NaOH$ is :
1. Mg 2. Al 3. Fe 4. Cu.

40. Which of the following is an efflorescent substance ?
1. Washing soda 2. Borax 3. Glauber salt 4. all the above.

41. Which of the following is a deliquescent substance ?
1. Caustic soda 2. Caustic potash 3. Common salt 4. all the above.

42. K_2CO_3 is not manufactured like Na_2CO_3 by Solvay process because.
1. K_2CO_3 is insoluble in water. 2. K_2CO_3 is less soluble in water than Na_2CO_3. 3. K_2CO_3 is more soluble in water than Na_2CO_3. 4. None.

43. Na when placed in air finally changes into :
1. $NaOH$ 2. Na_2O 3. Na_2CO_3 4. $NaCl$. **(MDAT 1981)**

44. Sodium is extracted by Castner's process from :
1. Washing soda 2. Caustic soda 3. $NaHCO_3$ 4. $NaCl$ 5. Chile saltpetre. **(PMDT 1976)**

45. In case of alkali metals :
1. the cation is less stable than the atoms.
2. the cation is smaller than the atom.
3. the cation and the atom have about the same size.
4. the cation is larger than the atom. **(NCERT 1981)**

□□□

CHAPTER 14

STUDY OF GROUP I-B OF ELEMENTS

(COPPER, SILVER, GOLD—COINAGE METALS)

14.1. Periodic Discussion

Copper, silver and gold are three transitional elements placed in I-B group of the periodic table. They are placed in the first group with alkali metals. Therefore, according to a new system, these elements are placed with other transitional elements of *d*-block. There is little similarity between the two sub-groups. Their electronic configurations are given below :

Coinage Metals :

Cu_{29}..2, 8, 18, 1 or $\boxed{Ar}\ 3d^{10}, 4s^1$

Ag_{47}..2, 8, 18, 18, 1 or $\boxed{Kr}\ 4d^{10}, 5s^1$

Au_{79}..2, 8, 18, 32, 18, 1 or $\boxed{Xe}\ 5d^{10}, 6s^1$

Alkali Metals :

Li_3..2, 1 or $\boxed{He}\ 2s^1$

Na_{11}..2, 8, 1 or $\boxed{Ne}\ 3s^1$

K_{19}..2, 8, 8, 1 or $\boxed{Ar}\ 4s^1$

Rb_{37}..2, 8, 18, 8, 1 or $\boxed{Kr}\ 5s^1$

By comparing this arrangement with alkali metals, we find that both sub-groups contain one electron in the outermost orbit but the penultimate orbit contains 18 electrons in I-B group elements and 8 electrons in I-A group elements. The removal of an electron from the atom of an alkali metal leaves a stable core of inert gas type having 8 electrons while in coinage metals the core contains 18 electrons. Hence one or more electrons may be withdrawn from the core for valence purposes. Thus coinage metals exhibit varible valency while alkali metals are uniformaly monovalent.

Another important characteristic of the metals of I-B group is that they form very stable complexes such as

$[Cu(NH_3)_4]^{++}$, $[Ag(CN)_2]^{-1}$ and $[AuCl_4]^{-}$

Moreover, this sub-group is characterized by the slight reactivity of the elements and the easy decomposition of the compounds.

14.2. Periodic Discussion

Copper, silver and gold constitute the sub-group I-B of the periodic table while *Li*, *Na*, *K*, *Rb*, *Cs* and *Fr* constitute the sub-group I-A. They are *transitional elements* of this group. The transitional elements of group VIII are placed on their left and *Zn*, *Cd* and *Hg* of sub-group II-B are placed on their right.

Their position in the periodic table is justified by the following facts :

(i) They, being members of the same sub-group, show marked similarity.

(ii) They show a regular gradation in their properties from *Cu* to *Au*.

(iii) They show a resemblance with the elements placed on their right and left.

Period	*Group I*		*Group II*		*Group VIII*
	A	*B*	*A*	*B*	
4th	K_{19}	Cu_{29}		Zn_{30}	Ni_{28}
5th	Rb_{37}	Ag_{47}		Cd_{48}	Pd_{46}
6th	Cs_{55}	Au_{79}		Hg_{80}	Pt_{78}

Resemblance :

(i) *Occurrence* : All are found in the free state in nature.

(ii) *Hard, malleable and ductile* : All are hard, malleable and ductile.

(iii) *Conductivity* : All are good conductors of heat and electricity.

(iv) *Density, melting point* and *boiling point* : All possess high density, melting point and boiling point.

(v) *Electronic configuration* : All possess similar electronic configuration as given below :

Cu_{29}..2, 8, 18, 1 or $\boxed{Ar}\ 3d^{10}4s^1$

Ag_{47}..2, 8, 8, 18, 1 $\boxed{Kr}\ 4d^{10}5s^1$

Au_{79}..2, 8, 18, 32, 18, 1 $\boxed{Xe}\ 5d^{10}6s^1$

All of them have one electron in the outermost orbit and 18 electrons in the penultimate orbit.

(vi) *Variable valency* : The core of all of these elements is unstable and one or more electrons may be withdrawn from it for valency. Thus copper gives cupurous Cu^+ (monovalent) and cupuric Cu^{++} (bivalent) ions.

Cu_{29}..2, 8, 18, 1 or $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10} 4s^1$
Cu^+..2, 8, 18 or $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}$
Cu^{++}..2, 8, 17 or $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^9$

Similarly, Gold gives aurous Au^+ and auric Au^{+++} (trivalent) ions.

Au_{79}..2, 8, 18, 32, 18, 1 or $\boxed{Xe}$
Au^+..2, 8, 18, 32, 18 (Aurous)
Au^{+3}..2, 8, 18, 32, 16 (Auric)

Cu^+ and Au^+ salts are unstable and their stable salts revert to Cu^{++} and Au^{+++} salts.

$$2Cu^+ \rightleftharpoons Cu + Cu^{++}$$
$$Cu_2SO_4 \rightleftharpoons CuSO_4 + Cu$$

and

$$3Au^+ \rightleftharpoons 2A + Au^{+++}$$
$$3AuCl \rightarrow 2Au + AuCl_3$$

(vii) *Combination with Chlorine* : All combine with Cl_2 to form chlorides. The metal in chlorides possess the higher valency.

$$(CuCl_2, AgCl, AuCl_3)$$

(viii) *Monovalent salts* : *Ag* forms mostly monovalent salts through a few bivalent compounds of silver are also known. Their monovalent salts are colourless and are generally insoluble in water.

$$(Cu_2Cl_2, AgCl, AuCl)$$

(ix) *Formation of complex ions* : All form complex salts in which the metal forms the part of cation or anion. For example :

$K[Ag(CN)_2]$ Pot. argentocyanide	$K_3[Cu(CN)_4]$ Pot. Cuprocyanide	$[Ag(NH_3)_2]Cl$ Silver amm. chloride
$K[Au(CN)_2]$ Pot. aurocyanide	$[Cu(NH_3)_4]SO_4$ Cupro amm. sulphate	$Na_3]Ag(S_2O_3)_2]$ Sodium Argento thiosulphate

(x) Their carbonates, acetates and nitrates generally decompose on heating e.g.

$$CuCO_3 \rightarrow CuO + CO_2$$
$$4AgNO_3 \rightarrow 2Ag_2O + 4NO_2 + O_2$$
$$Cu(CH_3COO)_2 \rightarrow CuCO_3 + CH_3COCH_3$$

(xi) *Displacement of the metals from their salts* : All the three metals can be displaced from their solutions by *Zn*, *Fe* or *Mg*.

$$CuSO_4 + Zn \rightarrow ZnSO_4 + Cu$$

Gradation :

These metals show a gradation in their properties as atomic number increases from Cu to Au.

(i) Density *increases* while specific heat decreases,

(ii) Malleability and ductility increase.

(iii) Electropositive nature and the chemical reactivity decrease. The last metal hardly forms a positive ion. It has a tendency to form covalent compounds.

(iv) Affinity for oxygen dininishes. Thus copper can form an oxide when heated in oxygen while Ag and Au are not attacked by it.

(v) Copper is readily attacked by acids, while silver is acted upon more slowly and gold is the least reactive.

(vi) Cu gives a large number of salts, Ag gives lesser while the salts of Au are the least.

(vii) Cuprous and aurous salts are not very stable and pass into cupric and auric salts the least in solution.

Relationship with Sub-group I-A. :

There is little resemblance between the two sub-groups except the monovalency. Silver resembles the alkali metals in the following properties :

(i) It gives colourless monovalent ion Ag^+ like Na^+.

(ii) Ag_2O is basic and slowly dissolves in water forming $AgOH$ which gives alkaline reaction.

(iii) It forms double salts of the composition of alums like

$$Ag_2SO_4\ Al_2(SO_4)_3.24H_2O.$$

Dissimilarities :

(i) The metals are inactive, noble and occur in the free state.

(ii) The oxides are not so basic as those of alkali metals.

(iii) They are much less reactive than alkali metals.

(iv) Their hardness, malleability, ductility and specific gravity are much higher than alkali metals.

(v) They form a large number of complex salts with ions such as

$$[Cu(NH_3)_4]^{++},\quad [Ag(CN)_2]^- \text{ etc.}$$

14.3. Copper

Symbol : Cu, *At. no.* 29, *At. Wt.* 63·54

Electronic configuration : $1s^2$, $2s^2\ 2p^6$, $3s^2\ 3p^6\ 3d^{10}$, $4s^1$.

Occurrence : It may be found in free state. Compounds of copper are distributed in nature as oxides, sulphides, carbonates etc. Some important ores of copper are given below :

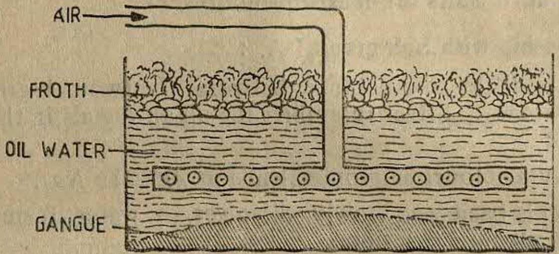
Copper glance....	Cu_2S
Copper pyrites....	$CuFeS_2$
Cuprite....	Cu_2O
Malachite....	$CuCO_3.Cu(OH)_2$
Azurite....	$2CuCO_3.Cu(OH)_2$

In India Copper ores are found in Bihar (Singhbhum), Orissa, Rajasthan (Khetri), Sikkim etc.

Extraction of Copper from Sulphide Ores :

The chief and important ore of copper from which the metal is mostly isolated is coppers pyrites ($CuFeS_2$). It is worked out by dry process involving the following steps :

(i) Concentration : The powdered ore is suspended in water and after adding little pine oil is stirred by means of air. The particles of the sulphide ore being preferentially wetted by the oil come to the surface along with the froth and are removed.



The gangue particles remain at the bottom and rejected.

(ii) Roasting : The concentrated ore is heated strongly in current of air on the hearth of reverberatory furnace whereby

(a) S is oxidised and removed as SO_2 oxides.

(b) *As* and *Sb* are removed as their volatile oxides.

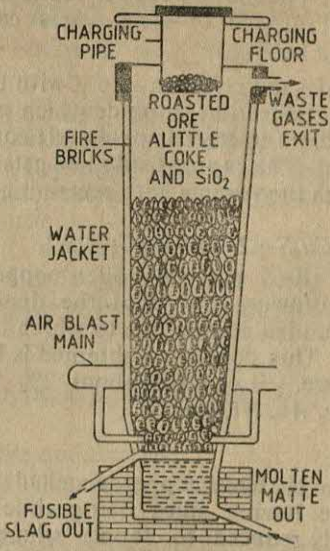
(c) The copper pyrite is partially converted into sulphide.

$$2CuFeS_2+O_2 \rightarrow Cu_2S+2FeS+SO_2$$

(d) The sulphides are further partially converted into oxides.

$$2Cu_2S+3O_2 \rightarrow 2Cu_2O+2SO_2$$
$$2FeS+3O_2 \rightarrow 2FeO+2SO_2$$

(iii) Smelting : The roasted ore ($Cu_2S+FeS+Cu_2O+FeO$) mixed with coke and sand is heated in water jacketted blast furnace. It is made up of steel plates lined inside with fire bricks. It is fitted up with tuyeres to admit blast of air.



Blast furnace

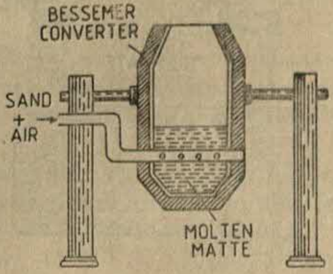
On heating, Cu_2S and FeS are partly converted into oxides. FeS is easily oxidised as iron has greater affinity for oxygen compared with copper. Moreover any Cu_2O formed combines with FeS to form more of ferrous oxide.

$$Cu_2O + FeS \rightarrow Cu_2S + FeO$$

Ferrous oxide combines with silica to form ferrous silicate, as slag.

$$FeO + SiO_2 \rightarrow FeSiO_3$$

The slag being lighter than molten mixture of Cu_2S and FeS called "*Copper Matte*" floats on the surface and is removed from the slag hole. The molten copper matte so obtained contains about 50% copper.



Bessemer's Converter

(iv) Bessemerisation : The molten copper matte is introduced into a small pear-shaped furnace of steel plates called "*Bessemer's converter.*"

A blast of air and sand is blown into it with the help of tuyeres from the side whereby the ferrous sulphide which escaped oxidation during smelting is oxidised to ferrous oxide. It combines with silica to form slag as before. The cuprous sulphide gets partially oxidised to cuprous oxide which then reacts with remaining sulphide to form copper.

$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$$

The converter is tilted and the molten copper is poured out in sand moulds. On allowing it to cool the dissolved SO_2 gas is given off from the solidified copper due to which blisters are produced on its surface. This copper so obtained is known as blistered copper and is 98% pure. It contains about 2% impurities consisting of As, Sn, Pb, Ag, Au, Ni, Zn etc.

Refining :

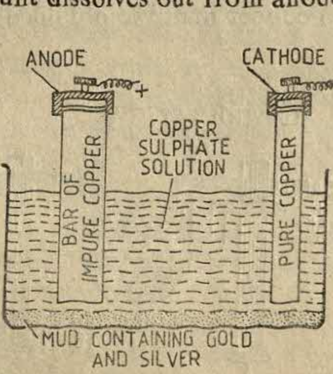
(a) *Poling* : (i) The blistered copper is melted on the hearth of reverberatory furnace having silica lining while the traces of Cu_2O present in it are mostly reduced to copper whereby the impurities are oxidised. These are either removed as gases or form slag with silica.

(ii) The fused metal is then fused with anthracite and stirred with poles of green wood when the hydrocarbon gases evolved reduce the traces of oxide into metal. It is 99·5% pure copper.

(b) **Electrolytic method** : This process consists of :

Cathode	Pure copper
Anode......	Impure copper
Electrolyte......	85% $CuSO_4$ containing 5% dil. H_2SO_4 taken is a lead lined tank.

On passing electric current, pure copper is deposited at cathode while the same amount dissolves out from anode. The most electro-



Refining of Copper

positive metals like *Fe, Ni, Zn* remain in solution while less electropositive metals like *Ag* and *Au* fall down below anode as *Anode mud.*

The metal so obtained is 99·9% pure and is now suitable for electrical purpose.

Wet process : In this process one of the metal is converted into soluble salts like chloride and sulphate by roasting or leaching with dil. H_2SO_4. The metal copper is then obtained from the solution either by electrolysis or by precipitation with more electropositive metal like iron.

$$CuSO_4+Fe\rightarrow FeSO_4+Cu$$

This method is mostly employed for extracting the metal from low grade sulphide ores or from non-sulphide ores.

Properties :

Physical : (i) Copper is a lustrous metal having a characteristic red colour.

(ii) It is malleable and ductile.

(iii) It is a very good conductor of heat and electricity being next to silver.

(iv) Its specific gravity is 8·95, melting point is 1083°C and boiling point is 2310°C.

(v) Molten metal has the property of occluding gases such as sulphur dioxide and hydrogen.

Chemical : **1. Action of Air** : Dry air has no action on the metal at ordinary temperature. When exposed to moist air and carbon dioxide it gets superficially coated with green carbonate called Virdigris. A film of green basic sulphate is also deposited by the action of the metal with SO_2 of the air.

$$2Cu+H_2O+CO_2+O_2\rightarrow Cu(OH)_2.CuCO_3$$
$$8Cu+6H_2O+2SO_2+5O_2\rightarrow 2[CuSO_4.3Cu(OH)_2]$$

2. Action of Heat : When heated in air, it gives a mixture of cuprous and cupric oxides.

$$4Cu+O_2\xrightarrow{\text{below }1100°C}2Cu_2O$$

$$2Cu+O_2\xrightarrow{\text{above }1100°C}2CuO$$

3. Action of Water : Water has no action on copper. It is slightly oxidised by steam only at white heat. The metal gets corrected by sea water.

4. Action of Acids : (i) Cold and dil. HCl or H_2SO_4 has no action on the metal but in presence of air and on warming the metal dissolves forming chloride and sulphate respectively.

$$2Cu+4HCl+O_2\rightarrow 2CuCl_2+2H_2O$$
$$2Cu+2H_2SO_4+O_2\rightarrow 2CuSO_4+2H_2O$$

(ii) It dissolves in hot conc. sulphuric acid evolving SO_2.

$$Cu+2H_2SO_4 \rightarrow CuSO_4+SO_2+2H_2O$$
$$(Cu+4H^{+}+SO_4^{-2} \rightarrow Cu^{+2}+SO_2+2H_2O)$$

(iii) Action with nitric acid :

(a) With cold and dil. HNO_3, nitrous oxide (N_2O) is evolved.

$$4Cu+10HNO_3 \rightarrow 4Cu(NO_3)_2+N_2O+5H_2O$$

(b) With warm and moderate HNO_3 (50%), nitric oxide (NO) is formed.

$$3Cu+8HNO_3 \rightarrow 3Cu(NO_3)_2+2NO+4H_2O$$

(c) With cold and conc. HNO_3, nitrogen peroxide (NO_2) is evolved.

$$Cu+4HNO_3 \rightarrow Cu(NO_3)_2+2NO_2+2H_2O.$$

(d) With hot and conc. nitric acid (vapour), nitrogen is evolved.

$$5Cu+2HNO_3 \rightarrow 5CuO+N_2+H_2O$$

5. **Action of Alkalis** : Alkalis have no action on the metal, but in presence of air, the metal dissolves in an aqueous solution of ammonia forming the complex salt, tetrammine copper hydroxide.

$$\begin{array}{c} Cu+H_2O+\tfrac{1}{2}O_2 \rightarrow Cu^{+2}+2OH^{-}\ [\times 2] \\ Cu^{++}+4NH_3 \rightarrow [Cu(NH_3)_4]^{++}[\ \times 2] \\ \hline 2Cu+2H_2O+O_2+8NH_3 \rightarrow 2[Cu(NH_3)_4]^{+2}+4OH^{-} \end{array}$$

6. **Action of Chlorine** : On heating with chlorine or other halogens, corresponding halide is formed.

$$Cu+Cl_2 \rightarrow CuCl_2$$

7. **Action with Sulphur, Seleniuum or Tellurium** : Copper combines with S, Se or Te forming the sulphide, selenide or telluride respectively.

$$Cu+S \rightarrow CuS$$

8. **Action with hydrobromic acid and hydroiodic acid** : With these acids copper forms complex salts.

$$2Cu+2HBr \rightarrow 2CuBr+H_2$$
$$2CuBr+2HBr \rightarrow H_2[CuBr_4]$$

9. **Displacement of metals** : Copper displaces silver, mercury and gold (less positive metals) from their salt solutions.

$$2AgNO_3+Cu \rightarrow 2Ag+Cu(NO_3)_2$$
$$HgCl_2+Cu \rightarrow Hg+CuCl_2$$

More electropositive metals displace copper from copper salt solution.

$$CuSO_4+Zn \rightarrow ZnSO_4+Cu\downarrow$$

10. **Reducing Agent** : Copper reduces ferric sulphate to ferrous sulphate.

$$Fe_2(SO_4)_3+Cu \rightarrow CuSO_4+2FeSO_4$$

Uses : (i) Due to its high electrical conductivity copper is used in making electrical cables, wires and other electrical goods.

(ii) For making coins.

(iii) In the preparation of copper salts which are largely used as insecticides.

(iv) In electroplating and electrotyping.

(v) In the manufactures of alloys e.g. brass, bronze, etc.

(vi) Being not easily attacked by air or water, it is used in making utensils, kettles, evaporating pans, water-bath etc.

Alloys of Copper

Alloy	*Composition*	*Uses*
1. Brass	$Cu = 60—80\%$ $Zn = 40—20\%$	Household utensils, Cartridges
2. Bronze	$Cu = 75—90\%$ $Sn = 25—10\%$	Utensils, coins and statues
3. Phosphorous Bronze	$Cu = 84—92\%$ $Sn = 5—6\%$ $P = 0{\cdot}25\%—2{\cdot}5\%$	Radio aerial wire, galvanometer etc.
4. German Silver	$Cu = 50\%$ $Zn = 25\%$ $Ni = 25\%$	Utensils and decoration articles
5. Gun-metal	$Cu = 87\%$; $Sn = 10\%$; $Zn = 3\%$	Guns, gears, castings etc.
6. Aluminium Bronze	$Cu = 80—90\%$ $Al = 7—12\%$ $Sn = 0{\cdot}05\%$	Coins; statue, golden paints, jewellery, cheap containers for corrosive liquids
7. Monel-metal	$Cu = 30\%$; $Ni = 67\%$ $Fe, Mn = 3\%$	Acid pumps and containers for acids
8. Bell-metal	$Cu = 80\%$; $Sn = 20\%$	Bell, gongs etc.

14.4. Compounds of Copper

Copper forms two series of compounds, *cuprous* (+I, O. S.) and *Cupric* (+2, O. S.). The cupric state is the most common and stable oxidation state. A few compounds containing copper (III) are known e.g. K_3CuF_6, but this oxidation state of copper is unimportant. The electronic configuration of copper, cuprous (Cu^+) and cupric (Cu^{++}) ions is shown below :

$$Cu(29) : 1s^2,\ 2s^2 2p^6,\ 3s^2 3p^6 3d^{10} 4s^1 ,(2K\ 8L,\ 18M,\ 1N)$$
$$Cu^+(29-1=28) : 1s^2,\ 2s^2 2p^6,\ 3s^2 3p^6 3d^{10}\ (2K,\ 8L,\ 8M)$$
$$Cu^{+2}(29-2=27) : 1s^2,\ 2s^2 2p^6,\ 3s^2 3p^6 3d^9\ (2K,\ 8L,\ 17M)$$

Cupric ions (Cu^{+2}) contain an unpaired electron in 3*d*-level, hence they are usually coloured and paramagnetic. If a cuprous salt is placed in water, disproportionation takes place :

$$2Cu^+ \rightleftharpoons Cu + Cu^{2+}$$

Hence aqueous solutions of cuprous ions are unstable. The cuprous ions (Cu^+) are, however, stabilized by complex formation.

In some cases cupric salts are unstable when the anion is easily oxidised e.g. (a) cupric iodide, (b) cupric cyanide and (c) cupric thiocyanate. In such cases, the cuprous salts are more stable than the corresponding cupric salts.

$$CuI_2 \rightleftharpoons Cu^{2+} + I^{-1} + I^- \rightleftharpoons \underset{\text{Cuprous iodide}}{CuI} + \tfrac{1}{2}I_2$$

$$Cu(CN)_2 \rightleftharpoons Cu^{2+} + CN^- + CN^- \rightleftharpoons \underset{\text{Cuprous cyanide}}{CuCN} + \tfrac{1}{2}(CN)_2$$

1. Copper (I) Oxide, Cuprous Oxide, Red Oxide of Copper, Cu_2O.

Preparation :

(i) It is obtained by heating cupric oxide with metallic copper.

$$CuO + Cu \rightarrow Cu_2O$$

(ii) By heating cuprous chloride with sodium carbonate.

$$Cu_2Cl_2 + Na_2CO_3 \rightarrow Cu_2O + 2NaCl + CO_2\uparrow$$

(iii) It is best prepared by reducing glucose with Fehling's solution.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{From Fehling soln.}}{2CuO} \rightarrow \underset{\text{Red}}{Cu_2O\downarrow} + \underset{\text{Gluconic acid}}{C_6H_{12}O_7}$$

Note : Fehling's solution is obtained by adding Rochelle salt (Sodium Potassium Tartarate) and excess of $NaOH$ solution to $CuSO_4$ solution. The deep blue coloured solution thus obtained is called Fehling's solution.

$$CuSO_4 + 2NaOH \rightarrow Na_2SO_4 + Cu(OH)_2$$
$$Cu(OH)_2 \rightarrow CuO + H_2O$$

Properties :

(i) It is red solid, insoluble in water. (ii) When heated in air, it is partly oxidised to cupric oxide.

(iii) *Reaction with acids* : (a) With nitric and sulphuric acids it forms cupric salts with the precipitation of free copper.

$$Cu_2O + 2HNO_3 \rightarrow Cu(NO_3)_2 + Cu\downarrow + H_2O$$
$$Cu_2O + H_2SO_4 \rightarrow CuSO_4 + Cu\downarrow + H_2O$$

(b) *With HCl*, cuprous chloride is formed which dissolves in excess of the acid, forming hydrocuprochloric acid, $H[CuCl_2]$.

$$Cu_2O + 2HCl \rightarrow 2CuCl + H_2O$$
$$2CuCl + 2HCl \rightleftharpoons 2H[CuCl_2]$$

(iv) *Reaction with carbon or hydrogen* : It is reduced by carbon or hydrogen.

$$(a)\ Cu_2O + C \rightarrow 2Cu\downarrow + CO;\quad (b)\ Cu_2O + H_2 \rightarrow 2Cu + H_2O$$

Uses : (i) In preparing anti rust paints. (ii) In making ruby red glass and enamel. (iii) In the manufacture of red pigment.

2. Copper (II) Oxide, Cupric Oxide (Black oxide of Copper CuO) :

Preparation :

(i) It is obtained by heating metallic copper strongly in air or oxygen.

$$2Cu + O_2 \rightarrow 2CuO$$

(ii) By heating the nitrate or the carbonate of copper.

$$2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2\uparrow$$
$$CuCO_3 \rightarrow CuO + CO_2\uparrow$$

(iii) On commercial scale it is made by heating the malachite,

$$CuCO_3.Cu(OH)_2 \rightarrow 2CuO + CO_2\uparrow + H_2O$$

Properties :

(i) It is a black solid, insoluble in water.

(ii) *Action of heat* : When heated above 1000°C it forms cuprous oxide.

$$4CuO \rightarrow 2Cu_2O + O_2\uparrow$$

(iii) *Action of hydrogen* : It is reduced on heating in a stream of hydrogen.

$$CuO + H_2 \rightarrow Cu + H_2O$$

(iv) *Action of acids* : It is basic oxide and forms salts with acids.

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O;\quad CuO + 2HNO_3 \rightarrow Cu(NO_3)_2 + H_2O$$

(v) *Action of Borax* : When fused with borax, it gives a blue mass of copper metaborate.

$$Na_2B_4O_7 \rightarrow 2NaBO_2 + B_2O_3$$
$$B_2O_3 + CuO \rightarrow Cu(BO_2)_2$$

Uses : (i) In the petroleum refining. (ii) For imparting blue or green colour glass. (iii) In the analysis of organic compounds for the estimation of carbon and hydrogen.

3. Copper (II) Hydroxide, Cupric Hydroxide, $Cu(OH)_2$:

Preparation : It is obtained when an aqueous solution of a cupric salt is made alkaline with caustic soda or Potash.

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2$$
$$CuSO_4 + 2NaOH \rightarrow Cu(OH)_2 + Na_2SO_4$$

Thus $Cu(OH)_2$. On decomposition at 80°C gives CuO.

Properties :

(i) It is a bluish-green gelatinous substance.

(ii) *Action of heat* : It decomposes to granular black cupric oxide on heating.

$$Cu(OH)_2 \rightarrow \underset{\text{Black}}{CuO} + H_2O$$

(iii) *Action of acids* : It reacts with acids to form salts and water.

$$Cu(OH)_2+H_2SO_4 \rightarrow CuSO_4+2H_2O$$
$$Cu(OH)_2+2HNO_3 \rightarrow Cu(NO_3)_2+2H_2O$$

(iv) *Action of ammonia* : It is readily soluble in an aqueous solution of ammonia with the formation of the intensely blue, tetrammino copper (ii) ion, $[Cu(NH_3)_4]^{2+}$.

$$Cu(OH)_2+4NH_3 \rightarrow [Cu(NH_3)_4](OH)_2$$

4. Copper (I) Chloride, Cuprous Chloride, $CuCl$ or Cu_2Cl_2 :

Preparation :

(i) It is prepared by the reduction of cupric chloride, with nascent hydrogen or SO_2.

$$2CuCl_2+2H \xrightarrow{Zn/HCl} Cu_2Cl_2+2HCl$$
$$CuCl+SO_2+2H_2O \rightarrow Cu_2Cl_2+H_2SO_4+2HCl$$

(ii) By heating a mixture of copper turnings and mercuric chloride.

$$2HgCl_2+Cu \rightarrow Cu_2Cl_2+Hg_2Cl_2$$

(iii) It is also obtained by passing SO_2 in a solution of copper sulphate and sodium chloride.

$$SO_2+2H_2O \rightarrow H_2SO_4+2\text{'}H\text{'}$$
$$\underline{2NaCl+2CuSO_4+2\text{'}H\text{'} \rightarrow Na_2SO_4+Cu_2Cl_2+H_2SO_4}$$
$$2NaCl+2CuSO_4+2H_2O+SO_2 \rightarrow Na_2SO_4+Cu_2Cl_2+2H_2SO_4$$

(iv) It is also prepared by heating cupric chloride, cupric oxide or sulphate with copper turnings and conc. hydrochloric acid until the green colour disappears. The solution is poured into water when a white precipitate of cuprous chloride is obtained.

$$CuCl_2+Cu \rightarrow Cu_2Cl_2\downarrow$$
$$CuO+Cu+2HCl \rightarrow Cu_2Cl_2\downarrow+H_2O$$
$$CuSO_4+Cu+2HCl \rightarrow Cu_2Cl_2\downarrow+H_2SO_4$$

Properties :

(i) It is a white crystalline, solid, insoluble in water. It melts at 422°C.

(ii) On exposure to air it is oxidised to cupric chloride.

(iii) Vapour density measurements of cuprous chloride show the vapour to be the dimer having the formula Cu_2Cl_2.

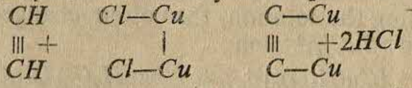
(iv) It dissolves in conc. HCl and NH_3 giving colourless solution.

$$Cu_2Cl_2+2HCl \rightarrow H_2Cu_2Cl_4 \rightarrow 2H[CuCl_2]$$

(v) In presence of conc. HCl colourless solution of Cu_2Cl_2 becomes blue on exposure to air due to the formation of cupric salts.

The oxidation of cuprous chloride into cupric chloride takes place readily in presence of $KMnO_4$ (oxidising agent).

(vi) Ammoniacal solution of cuprous chloride forms a red precipitate of cuprous acetylede when acetylene is passed.



$$\begin{array}{ccccc} CH & & Cl-Cu & & C-Cu \\ ||| & + & | & \rightarrow & ||| \quad +2HCl \\ CH & & Cl-Cu & & C-Cu \end{array}$$

(vii) *Sandmeyer reaction* : When benzene di-azonium chloride is treated with cuprous chloride and hydrochloric acid, chlorobenzene is formed.

(viii) Carbon monoxide dissolves in ammoniacal cuprous chloride forming an addition compound, $CuCl.\ COH_2O$.

(ix) It reacts with $NaOH$ and H_2S forming cuprous oxide and cuprous sulphide respectively.

Uses : (i) Its ammoniacal solution is used in absorbing CO and C_2H_2.

(ii) It is used along with NH_4Cl as a catalyst in the dimerization of acetylene into vinyl acetylene.

5. Copper (II) Chloride, Cupric Chloride, $CuCl_2.2H_2O$:

Preparation :

(i) It is prepared by dissolving copper in aqua regia or its oxide, hydroxide or carbonate in HCl. The solution on evaporation gives green crystals of $CuCl_2.2H_2O$

(a)

$$\begin{array}{c} 3HCl+HNO_3 \rightarrow NOCl+2H_2O+2\text{‘}Cl\text{’} \\ Cu+2\text{‘}Cl\text{’} \rightarrow CuCl_2 \\ \hline Cu+3HCl+HNO_3 \rightarrow CuCl_2+NOCl+2H_2O \end{array}$$

(b)

$$CuO+2HCl \rightarrow CuCl_2+H_2O$$

$$CuCO_3+2HCl \rightarrow CuCl_2+H_2O+CO_2\uparrow$$

(ii) *Anhydrous* cupric chloride is obtained when copper is heated in chlorine.

$$Cu+Cl_2 \rightarrow CuCl_2$$

Anhydrous cupric chloride can also be obtained by heating the hydrated $CuCl_2.2H_2O$ in a current of HCl gas at 150°C.

It can also be obtained by heating the hydrated chloride with thionyl chloride.

$$CuCl_2.2H_2O+2SOCl_2 \rightarrow CuCl_2+4HCl+2SO_2$$

Properties :

(i) It is a green crystalline solid, soluble in water.

(ii) *Action of heat* : When heated it first becomes anhydrous and decomposes on further heating.

$$2CuCl_2 \rightarrow Cu_2Cl_2+Cl_2$$

(iii) *Action of water* : An aqueous solution of Cupric chloride (and all cupric salts) is blue to the hydrated ion $[Cu(H_2O)_6]^{2+}$.

$$CuCl_2 \rightleftharpoons Cu^{2+} + 2Cl^-$$
$$Cu^{2+} + 6H_2O \rightarrow \underset{\text{Blue hydrated } Cu^{2+} \text{ ion}}{[Cu(H_2O)_6]^{2+}}$$

On addition of conc. HCl or the chloride of the alkali metals or even concentrating the solution, the colour changes to green due to the formation of $[CuCl_4]^{2-}$ ion.

$$\underset{\text{Blue}}{[Cu(H_2O)_6]^{2+}} + 4Cl^- \rightleftharpoons 6H_2O + \underset{\text{Green}}{[CuCl_4]^{2-}}$$

(iv) It is a *covalent* compound.

(v) *Action of ammonia* : Its solution, when reacts with ammonium hydroxide gives a precipitate of cupric hydroxide, which dissolves in excess of the reagent giving deep blue solution due to the formation of complex tetrammine copper (ii) ions $[Cu(NH_3)_4]^{2+}$. The solution on evaporation forms deep blue crystals of tetrammine Cupric chloride, $[Cu(NH_3)_4]\ Cl_2.H_2O$.

$$CuCl_2 + 2NH_4OH \rightarrow Cu(OH)_2 + 2NH_4Cl$$
$$Cu(OH)_2 + 2NH_4Cl + 2NH_4OH \rightarrow [Cu(NH_3)_4]Cl_2 + 4H_2O$$

With NH_3, it forms various compounds e.g. $CuCl_2.6NH_3$; $Cu_2Cl_2.2NH_3$.

6. Cuprous Bromide, Copper (I) Bromide, $CuBr$, Cu_2Br_2. :

It can be prepared by a method similar to that used for making cuprous chloride. It resembles cuprous chloride in many respects.

7. Cupric Bromide, Copper (II) Bromide, $CuBr_2$:

Cupric bromide is a black crystalline solid which resembles chloride in many respects.

8. Cuprous Iodide, Copper (I) Iodide, CuI, Cu_2I_2

Cupric iodide, CuI_2, is not known. Cuprous iodide is precipitated when a solution of KI is added to a solution of cupric salt such as copper sulphate.

$$2CuSO_4 + 4KI \rightarrow 2CuI_2 + 2K_2SO_4$$
$$2CuI_2 \rightarrow Cu_2I_2 + I_2$$
$$\overline{2CuSO_4 + 4KI \rightarrow Cu_2I_2 + I_2 + 2K_2SO_4}$$

The reaction can be used to estimate Cu^{2+} ions.

In the above reaction, the brown colour of the solution is due to precipitated iodine. However, if the reaction takes place in presence of a reducing agent such as SO_2 gas or ferrous sulphide, Iodine is set free and cuprous iodide is precipitated as a white mass.

$$2CuSO_4 + 2KI + SO_2 + 2H_2O \rightarrow Cu_2I_2 + 2KHSO_4 + H_2SO_4$$

It is a white crystalline powder, insoluble in water. It is not oxidised by air.

9. Copper (II) Iodide, Cupric Iodide, CuI_2 :

It is unstable compound, an attempt to prepare cupric iodide results in the formation of cuprous iodide.

10. Copper (II) Sulphate, Cupric Sulphate, $CuSO_4.5H_2O$ (Blue vitriol).

Preparation :

(i) It is formed by the action of hot and conc. H_2SO_4 on copper.

$$Cu+2H_2SO_4 \rightarrow CuSO_4+SO_2+2H_2O$$

The solution on crystallisation gives crystal of $CuSO_4.5H_2O$.

(ii) It is also obtained by dissolving copper oxide, hydroxide or carbonate in dilute sulphuric acid.

$$CuO+H_2SO_4 \rightarrow CuSO_4+H_2O$$
$$CuCO_3+H_2SO_4 \rightarrow Cu(SO_4)+H_2O+CO_2\uparrow$$

(iii) On large scale, it is prepared by blowing air through a hot mixture of dilute sulphuric acid and copper scrap.

$$2Cu+2H_2SO_4+O_2 \rightarrow 2CuSO_4+2H_2O$$

(iv) *Action of ammonia* : If ammonia is added to a solution of copper sulphate cupric hydroxide is precipitated which dissolves in excess of ammonia forming a deep blue solution due to the complex substance, Tetramirine $Cu(II)$ sulphate $[Cu(NH_3)_4]SO_4$.

(v) *Action of sodium thiosulphate solution* (Hypo) : It reacts with hypo to give sodium cuprothiosulphate.

$$CuSO_4+Na_2S_2O_3 \rightarrow Na_2SO_4+CuS_2O_3$$
$$2CuS_2O_3+2Na_2S_2O_3 \rightarrow \underset{\text{Sod. cuprothiosulphate}}{2NaCuS_2O_3} + Na_2S_4O_6$$

(vi) *Action of KI solution* : When KI solution is added to copper sulphate solution then white precipitate of Cuprous Iodide is obtained and brown I_2 is liberated.

$$\begin{array}{c} CuSO_4+2KI \rightarrow CuI_2+K_2SO_4\ [\times 2] \\ 2CuI_2 \rightarrow Cu_2I_2+I_2 \\ \hline 2CuSO_4+4KI \rightarrow Cu_2I_2+I_2+K_2SO_4 \end{array}$$

(vii) *Action of KCN* (Potassium Cyanide) : On adding KCN solution to a solution of copper sulphate then cuprous cyanide is formed which dissolves in excess of the reagent forming Potassium cuprocyanide.

$$\begin{array}{l} 2CuSO_4+4KCN \rightarrow 2CuCN\downarrow+(CN)_2+2K_2SO_4 \\ CuCN+3KCN \rightarrow K_3[Cu(CN)_4\ [\times 2] \\ \hline 2CuSO_4+10KCN \rightarrow 2K_3[Cu(CN)_4]+2CuCN+(C_2N_2)+2K_2SO_4 \end{array}$$

Manufacture : In this case dilute sulphuric acid is sprayed on fine scrap copper placed in a lead-lined tower in which air is blown upwards from the bottom. The solution so obtained is circulated until a concentrated solution of copper sulphate is obtained, which on evaporation gives blue crystals of copper sulphate.

Properties :

(i) It is a blue crystalline solid, soluble in water.

(ii) *Action of heat* : It looses 4 molecules of water of crystallisation at 100°C and at 230°C white anhydrous copper sulphate is formed. This white anhydrous copper sulphate turns to blue copper sulphate $CuSO_4, 5H_2O$ in contact with water.

$$\underset{\text{Blue}}{CuSO_4.5H_2O} \xrightarrow{100°C} CuSO_4.H_2O + 4H_2O$$

$$CuSO_4.H_2O \xrightarrow{230°C} \underset{\text{White}}{CuSO_4} + H_2O$$

$$CuSO_4 \xrightarrow{736°C} CuO + SO_3$$

(iii) *Action of alkalis, MOH ($M = Na, K$)* : A blue green gelatinous precipitate is obtained when an aqueous solution of copper sulphate is made alkaline with $NaOH$ or KOH.

$$CuSO_4 + 2NaOH \rightarrow \underset{\text{Bluish green}}{Cu(OH)_2\downarrow} + Na_2SO_4$$

Cupric hydroxide slightly dissolves in concentrated alkali due to the formation of the complex ion $[Cu(OH)_4]^{2-}$.

$Cu(OH)_2 + 2OH^- \rightleftharpoons [Cu(OH)_4]^{2-}$ (Cuprite ion→unstable)

e.g. $Cu(OH)_2 + 2NaOH \rightleftharpoons Na_2[Cu(OH)_4]$

(iii) *Action Potassium thiocyanate solution* : When $KSCN$ is added to copper sulphate solution, white precipitate of cuprous thiocyanate is obtained.

$$pCuSO_4 + 4KSCN \rightarrow \underset{\text{white}}{2CuSCN\downarrow} + 2K_2SO_4 + (SCN)_2\uparrow$$

(iv) *Action of H_2S* : When H_2S is passed into solution of copper sulphate then black precipitate of cupric sulphide is obtained.

$$CuSO_4 + H_2S \rightarrow \underset{\text{Black}}{Cus\downarrow} + H_2SO_4$$

(v) *Displacement reaction* : On addition of zinc or iron, copper being less electropositive (+ve) gets precipitated.

$$CuSO_4 + Fe \rightarrow FeSO_4 + Cu$$

Uses : (i) As a germicide in agriculture. (ii) In preparation of green pigments. (iii) As mordant in dying and calico printing, (iv) In copper plating, electroplating and electrorefining of copper. (v) Anhydrous salt is used in detecting the presence of moisture in sample of absolute alcohol.

Note : In $CuSO_4.5H_2O$ four out of the five water molecules are associated with the cation and the fifth with the anion.

$$[Cu(H_2O)_4]SO_4.H_2O$$

Hence 4 molecules of water are easily removed at 100°C and one molecule of H_2O is removed at 230°C. Therefore, $CuSO_4.5H_2O$ contains 4 molecules of water of crystallisation and one molecule of water of constitution.

11. Cupric Nitrite, $Cu(NO_2)_2$:

It is an unstable solid, but it is stable in solution. It is formed by the action of silver nitrite on cupric chloride or by the action of barium nitrite on copper sulphate solution.

$$CuSO_4+Ba(NO_2)_2\rightarrow BaSO_4\downarrow+Cu(NO_2)_2$$

12. Cupric Nitrate, $Cu(NO_3)_2.3H_2O$:

Preparation :

It is prepared by dissolving the metal oxide, hydroxide or carbonate in dilute nitric acid and crystallising the solution by evaporation.

$$CuO+2HNO_3\rightarrow Cu(NO_3)_2+H_2O$$
$$Cu(OH)_2+2HNO_3\rightarrow Cu(NO_3)_2+H_2O+CO_2$$

Properties :

(i) It is a deep blue crystalline solid, deliquescent in nature, soluble in water.

(ii) On heating to 66°C it becomes anhydrous and on further heating decomposes to form cupric oxide oxygen and nitrogen dioxide.

$$2Cu(NO_3)_2\rightarrow 2CuO+4NO_2\uparrow+O_2\uparrow$$

13. Cupric Carbonate, $CuCO_3$:

The normal carbonate is unknown. Addition of Na_2CO_3 or $NaHCO_3$ solutions to a solution of copper (II) salt results in the formation of green basic salt of formula $2CuCO_3.Cu(OH)_2$.

14. Basic Copper Acetate (Verdigris), $Cu(CH_3COO)_2.Cu(OH)_2$:

Preparation :

It is prepared by exposing thin sheets of copper to the action of vinegar and air.

$$2Cu+2CH_3COOH+O_2\ (\text{air})\rightarrow Cu(CH_3COO)_2.Cu(OH)_2$$

Properties :

(i) It is greenish blue powder, insoluble in water.

(ii) It is soluble in dilute acids and ammonia.

Uses : It is used in the manufacture of green paints because of its green colour, good covering power and unaffected by light.

Detection of Copper salts

Dry test :

(a) *Borax Bead test* : Blue bead in oxidising flame and red bead in Reducing flame.

(b) Fusion with sodium carbonate on charcoal block gives a reddish brown residue of copper.

Wet Test : Copper (II) Ions :

Ammonia gives a pale blue precipitate dissolving in excess of NH_3, forming a deep blue solution of tetrammine copper (II) ion.

Estimation of Copper :

(a) *Volumetric estimation* : Copper is estimated volumetrically by treating the cupric salt with excess of KI. The liberated iodine is titrated with standard sodium thiosulphate solution.

$$Cu^{2+} \equiv I_2 \equiv Na_2S_2O_3$$

(b) *Gravimetric estimation* : Cupric salt solution containing sulphate is treated with ammonium thiocyanate solution whereby cuprous thiocyanate is precipitated.

$$2CuSO_4 + SO_2 + 2H_2O + 2NH_4CNS \rightarrow 2CuCNS + 2H_2SO_4 + (NH_4)_2SO_4$$

The precipitate is dried at 110°-120°C and weighed as the thiocyanate.

14.5. Silver :

Symbol : *Ag*, *At. No.* 47, *At. wt.* 107. 87

Electronic configuration :

$$1s^2, 2s^2 3p^6, 3s^2 3p^6 {}_3d^{10} 4s^2 4p^6 4d^{10} 5s^1$$

Occurence : It occurs in free state. Some important ores are given below.

(i) Ruby Silver or (Pyrogyrite) .... $3Ag_2S. Pb_2S_3$
(ii) Silver glance or (Argentite) .... Ag_2S
(iii) Horn silver or (Chlorapytite) .... $AgCl$

The chief and important of these is silver glance Ag_2S which is present as such or is associated with galena, PbS.

Extraction of Silver :

1. *Amalgamation Process* : The powdered ore containing Ag_2S is thoroughly stirred with water and cupric chloride when silver sulphide is converted into silver chloride.

$$2CuCl_2 + Ag_2S \rightarrow Cu_2Cl_2\downarrow + 2AgCl\downarrow + S$$

This product is mixed with mercury which displaces silver and forms silver amalgam.

$$2AgCl + 2Hg \rightarrow 2Ag\downarrow + Hg_2Cl_2$$

This is washed and distilled, when mercury (b.p. 377°) distills over leaving silver (b.p. 1970°) behind.

2. *Desilerisation of Crude'Lead* :

Galena *PbS*, an important ore of lead contains a very small amount of Ag_2S also and is commonly known as argentiferrous galena. The metal lead obtained from this ore thus contains a small quantity of silver as well which is separated by two main process.

(a) *Park's Process (1850)* : This is based on the following facts :

(i) Molten zinc and lead are not miscible and form two separate layers. The upper layer is that of zinc.

(ii) Silver is more soluble in molten zinc than in molten lead.

(iii) *Zn-Ag* alloy has higher melting point than that of lead and is lighter than molten lead.

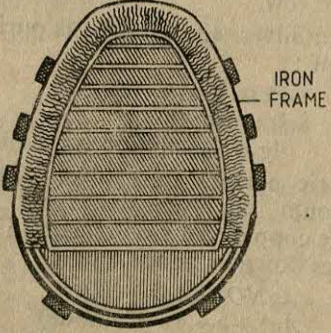
In actual practice crude lead containing silver is melted and molten zinc (1%) is added to it. It is thoroughly stirred and allowed to stand when zinc containing whole of silver forms an upper layers. On allowing it to cool, the *Zn-Ag* Alloy solidifies and floats on the surface of molten lead. The alloy is skimmed off with perforated spoons and is then distilled in retort. Zinc being more volatile (b.p. 907°) than silver (b.p. 1970°) distills over leaking behind silver.

(b) *Pattinson's Process (1833)* : It is based on the fact that melting point of *Pb-Ag* alloy is less than that of pure lead. Thus when crude lead containing silver is melted and allowed, to cool, lead crystallises out while the percentage of silver in the mother liquor increases. The mother liquor is separated, again melted and cooled. More of lead separates out. The process is repeated till most of lead removed from silver.

The method is, however, not very satisfactory and has almost been given up.

Purification. The silver obtained by the above process contains lead as an impurity and is purified by :

Cupellation. The impure silver is taken in a shallow bone ash dish called cupel and is fused on the hearth of cupellation furnace.



A current of air is blown over it when lead is oxidised to PbO which is partly blown away by air and partly absorbed by the porous material of the cupel. The end of the process is indicated by the appearance of shining surface of silver.

3. *Gyanide Process* (*Mac Arthur Forrests*) Process, (1877). The fine by powdered ore after being concentrated by froth floatation process is treated with dilute (0·7%) $NaCN$ solution and a current of air is blown into it. The silver present in the ore dissolves forming a complex soluble salt sodium argentocyanide.

$$Ag_2S+2NaCN\rightarrow 2AgCN+Na_2S$$
$$\underline{AgCN+NaCN\rightarrow Na[Ag(CN)_2][\times 2]}$$
$$Ag_2S+4NaCN\rightarrow 2Na[Ag(CN)_2]+Na_2S$$

or
$$Ag_2S+4CN^-\rightarrow 2[Ag(CN)_2]^{-1}+S^{-2}$$

The reaction is reversible and in order to prevent backward reaction it is essential to remove sodium sulphide from the sphere of action. The oxygen of the air converts sodium sulphide into sodium sulphate and free sulphur and thus makes the above reaction is irreversible.

$$4Na_2S+5O_2+2H_2O\rightarrow 2Na_2SO_4+4NaOH+2S$$

In case the ore is silver chloride then, too, it goes into solution forming sodium argentocyanide.

$$AgCl+2NaCN\rightarrow Na[Ag(CN)_2]+NaCl$$

or
$$AgCl+2CN^-\rightarrow [Ag(CN)_2]^{-1}+Cl^{-1}$$

The solution of sodium argentocyanide, obtained as above, is treated with finally powdered zinc. Zinc being more electro+*ve* than silver displaces it from the solution. A black precipitate of silver is thus obtained.

$$2Na[Ag(CN)_2]+Zn\rightarrow Na_2[Zn(CN)_4]+2Ag$$

The precipitated silver is mixed with potassium nitrate and fused when the impurities are oxidised and removed as a scum from the surface of molten metal. On cooling a compact shining mass of silver is formed.

This is the best method of extracting silver from its ore especially when the % of silver is low.

Refining of silver: Silver so obtained is purified by electrolytic process. It consists of :

Cathode	Pure Ag
Anode	Impure Ag
Electrolyte	$AgNO_3$ solution containing 1% HNO_3

On passing electric current pure silver is deposited on cathode while the same amount dissolves out from anode. The more electro+*ve* metals like copper and zinc remain in solution while less electro+*ve* gold comes down as anode mud.

Reactions :
$$AgNO_3\rightleftharpoons Ag^++NO_3^{-1}$$
$$Ag^++e\rightarrow Ag \text{ (Cathode)}$$
$$NO_3^-+Ag^+\rightarrow AgNO_3+e \text{ (Anode)}$$

Silver from Bazar Silver (or Coin containing Copper and Silver) : The coin containing copper and silver is treated with dilute HNO_3 when both copper nitrate and silver nitrate are formed in the solution. Dil. HCl is added to it when white precipitate of $AgCl$ is formed which is separated by filtration.

$$3Ag+4HNO_3 \rightarrow 3AgNO_3+NO+2H_2O$$
$$AgNO_3+HCl \rightarrow AgCl\downarrow+HNO_3$$
$$3Cu+8HNO_3 \rightarrow 3Cu(NO_3)_2+2NO+4H_2O$$
$$Cu(NO_3)_2+2HCl \rightarrow \underset{\text{Solution}}{CuCl_2}+2HNO_3$$

The precipitate ($AgCl$) is either fused with Na_2CO_3 or reduced with nascent hydrogen evolved by zinc and dil. H_2SO_4 to get metal silver.

(i) $AgCl+2Na_2CO_3 \rightarrow 4NaCl+4Ag+2CO_2+O_2$

(ii) $Zn+H_2SO_4 \rightarrow ZnSO_4+2\text{'}H\text{'}$

$AgCl+\text{'}H\text{'} \rightarrow Ag\downarrow+HCl.$

Properties of Silver :

Physical : (i) Silver is a lustrous white metal.

(ii) It is a heavy metal, sp. gr. 10·5

(iii) It is highly melleable and ductile.

(iv) It is the best conductor of heat and electricity.

(v) It melts at 960°C and boils at 1954·9°C.

(vi) Molten silver absorbs '20-25 times of its volume of oxygen, which is given out on cooling. This is known as *spitting of silver.*

Chemical :

1. *Action of air* : Pure air has no action on the metal. It is blackened when air contains traces of H_2S

$$H_2S+2Ag \rightarrow Ag_2S+H_2$$

For similar reason silver cutlery is tarnished by good articles rich in sulphur.

2. *Action with Ozone*: Silver reacts with ozone at ordinary temperature to form silver peroxide.

3. *Action with Chlorine* : Silver directly combines with halogens to form halides

$$2Ag+Cl_2 \rightarrow 2AgCl$$

4. *Action with acids* : (a) Dilute HCl and Dil. H_2SO_4 have no action on silver.

(b) Nitric acid hot or cold, dilute or concentrated dissolves the metal forming silver nitrate and nitrogen oxides.

$$3Ag+4HNO_3\text{ (dilute)} \rightarrow 3AgNO_3+NO+2H_2O$$
$$Ag+2HNO_3\text{ (conc.)} \rightarrow AgNO_3+NO_2+H_2O$$

(c) When heated with conc. H_2SO_4, it evolves Sulphur dioxide

$$2Ag+2H_2SO_4 \rightarrow Ag_2SO_4+SO_2+2H_2O.$$

5. *Action with Alkalies* : Alkalies have no action on silver even when fused.

Uses : It is used

(i) For making coins, jewellery and decorative articles.
(ii) In electroplating, silvering in mirrors.
(iii) In preparing photographic film and plates.
(iv) In dentistry in filling teeth.
(v) In Aurvedic medicine as a tonic.

14.6. Compounds of Silver

1. Silver (I) Chloride, Argentous chloride, *AgCl*. It occurs in nature as horn silver.

Preparation

(i) It is easily obtained as a white precipitate by adding the solution of a chloride or dil. HCl to silver salt solution.

$$AgNO_3+NaCl\rightarrow AgCl\downarrow+NaNO_3$$
$$Ag^++Cl^-\rightarrow AgCl$$

(ii) It is also formed by passing chlorine over heated silver.

$$2Ag+Cl_2\rightarrow 2AgCl$$

Properties

(i) It is a white solid insoluble in water and dil. acids.

(ii) *Action of heat* : On exposure to air it turns violet, brown and finally black due to decomposition. On heating to 450°C it turns to a yellow liquid.

(iii) *Action of (a) ammonia (b) Alkali Cyanides (c) Sodium thiosulphates.*

(a) Silver chloride absorbs ammonia forming $2AgCl.\ 3NH_3$ and $AgCl\ 2NH_3$. when ammonia solution is added to silver chloride then $AgCl$ is dissolved giving $[Ag(NH_3)_2]\ Cl$ (complex). This gives $AgCl$ when it is treated with HNO_3

$$AgCl\ (\text{White})+2NH_4OH\rightarrow[Ag(NH_3)_2]Cl\ (\text{Solution})+2H_2O$$
$$[Ag(NH_3)_2]Cl+HNO_3^-\rightarrow AgCl\downarrow+2NH_4NO_3$$

(b) $AgCl$ gives alkali argentocyanide with $NaCN$ or KCN solution.

$$AgCl+2MCN\rightarrow M[Ag(CN)_2]+MCl\ (M=Na,K)$$

(c) $AgCl$ gives sodium argentothiosulphate with sodium thiosulphate.

$$AgCl+2Na_2S_2O_3\rightarrow Na_3\ [Ag(S_2O_3)_2]+NaCl.$$

(iv) *Action of Potassium Bromide and iodide* : It is converted to silver bromide or iodide when left in contact with solutions of KBr or KI respectively.

$$AgCl+KBr\rightarrow KCl+AgBr\downarrow$$
$$AgCl+KI\rightarrow KCl+AgI\downarrow$$

(iv) *Action of Sodium or Potassium carbonate*: When silver chloride is fused with sodium or potassium carbonate then metallic silver is formed. ($M=Na, K$)

$$4AgCl+M_2CO_3 \rightarrow 4Ag+4MCl+2CO_2\uparrow+O_2 (M=Na, K)$$

(v) *Action of hydrogen*: It is reduced to metallic silver when it is heated in a current of hydrogen.

$$2AgCl+H_2 \rightarrow 2Ag+2HCl$$

(vi) *Action of Zinc*: Silver chloride is reduced to silver by zinc in presence of dilute acids.

$$2AgCl+Zn \rightarrow 2Ag+ZnCl_2$$

(vii) *Action of HCl*: Silver chloride is insoluble in dilute HCl but its solubility increases as the concentration of acid increases due to the formation of the complexion.

$$AgCl+HCl \rightleftharpoons H[AgCl_2] \rightleftharpoons H^+ + [AgCl_2]^{-1}$$

Uses: It is used extensively in photography.

2. Silver (I) Bromide, Argentous Bromide, *AgBr*.

Preparation

It is obtained as a pole cream solid by the action of solution of a soluble Bromide on silver salts.

$$AgNO_3+NaBr \rightarrow AgBr+NaNO_3$$

Properties

(i) It is insoluble in water and conc. acids. (ii) It is soluble in concentrated NH_4OH and hypo or KCN solution forming complex salts.

(a) $AgBr+2NH_4OH \rightarrow [Ag(NH_3)_2]\ Br+2H_2O$

(b) $AgBr+2KCN \rightarrow K[Ag(CN)_2]+KBr$

(c) $AgBr+2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2]+NaBr.$

On heating it melts to a red liquid. It gives $AgCl$ when chlorine is passed over it.

Uses: It is used in photography.

3. Silver (I) Iodide, Argentous Iodide, *AgI*.

Preparation

It may be obtained by adding a soluble iodide to a silver salt solution.

$$NaI+AgNO_3 \rightarrow AgI+NaNO_3$$

Properties

(i) It is yellow solid, insoluble in water, conc. acids and even in NH_4OH.

(ii) It is soluble in liquid ammonia forming $Ag\,NH_3.I$. It is also soluble in conc. KCN solution forming pot. argentocyanide.

$$AgI+KCN \rightarrow K[Ag(CN)_2]$$

(iii) On passing Cl_2 silver chloride is formed.

$$2AgI+Cl_2 \rightarrow 2AgCl+I_2$$

Uses : It is used in photography.

4. Silver Nitrate (Lunar caustic), $AgNO_3$

Preparation

It is prepared by dissolving silver in dilute nitric acid in a porcelain or stainless steel container. The solution is evaporated till crystals of silver nitrate appear.

$$3Ag+4HNO_3(\text{Dil.}) \rightarrow 3AgNO_3+2H_2O+NO\uparrow$$
$$Ag+2HNO_3(\text{Conc.}) \rightarrow AgNO_3+H_2O+NO_2\uparrow$$

The salt is purified by recrystallisation from distilled water.

Properties

(i) Silver nitrate forms colourless anhydrous ehombic crystals which are extremely soluble in water.

(ii) It is also called as *Lunar caustic* because it burns the skin (caustic) and because it gives silver which is white like the moon (luna).

(iii) *Action of heat* : It melts at 218°C and at 450°C it decomposes into silver nitrite, $AgNO_2$, which on stronger heating decomposes into silver.

$$2AgNO_3 \rightarrow 2AgNO_2+O_2\uparrow$$
$$2AgNO_3 \rightarrow 2Ag+2NO_2+O_2\uparrow$$

(iv) *Action of ammonia* : It dissolves in aqueous solution of ammonia forming the complex ion, $[Ag(NH_3)_2{}^+$

$$AgNO_3+2NH_3 \rightleftharpoons [Ag(NH_3)_2]NO_3 \rightleftharpoons [Ag(NH_3)_2]^+ + NO_3{}^{-1}$$

Ammonical silver nitrate is known as *Tollen's reagent*. Ammonical silver nitrate is readily reduced to silver by many organic agents, such as aldehydes, formates, sugars etc.

$$2[Ag(NH_3)_2]NO_3+\underset{\text{Glucose}}{C_6H_{12}O_6}+H_2O \rightarrow 2Ag\downarrow+\underset{\text{Gluconic acid}}{C_6H_{12}O_7}+2NH_4NO_3+2NH_3$$

Ammonical $AgNO_3$ reacts with acetyline giving a white precipitate of silver acetylide.

$$C_2H_2+2[Ag(NH_3)_2]NO_3 \rightleftharpoons \underset{\text{white}}{Ag_2C_2}+2NH_4NO_3+2NH_3$$

(v) *Action of soluble halides* : When a solution of a metal halide (except fluorine, because AgF is soluble) is treated with $AgNO_3$ solution, then corresponding halides are precipitated.

$$NaCl+AgNO_3 \rightarrow AgCl\downarrow(\text{white})+NaNO_3$$
$$NaBr+AgNO_3 \rightarrow AgBr\downarrow(\text{yellow})+NaNO_3$$
$$NaI+AgNO_3 \rightarrow AgI\downarrow(\text{yellow})+NaNO_3.$$

Hence $AgNO_3$ is used for the detection and quantitative estimation of halide.

(vi) *Action of organic acid* : The silver salts of organic acids are obtained as white precipitates on adding silver nitrate to a neutral solution of the acid.

$$R.COOH+NaOH \rightarrow R.COONa+H_2O$$
$$R.COONa+AgNO_3 \rightarrow \underset{\text{White}}{R.COO^- Ag^+\downarrow}+NaNO_3$$

(vii) *Action of alkali* : Silver nitrate solution gives a precipitate of Ag_2O with cuastic alkalies.

$$2AgNO_3+2NaOH \rightarrow Ag_2O+2NaNO_3+H_2O$$

(viii) *Action of soluble salts* : Silver nitrate solution reacts with cyanide, thiocyanates, caronate, chromates etc. to give the precipitates of corresponding salts.

$$AgNO_3+KCN \rightarrow AgCN\downarrow+KNO_3$$
$$AgNO_3+NaSCN \rightarrow AgSCN\downarrow+NaNO_3$$
$$2AgNO_3+Na_2CO_3 \rightarrow Ag_2CO_3\downarrow+2NaNO_3$$
$$2AgNO_3+K_2CrO_4 \rightarrow AgCrO_4\downarrow+2KNO_3$$

Uses :

(i) It is used as a laboratory reagent.

(ii) In the preparation of silver halides which are used in photography.

(iii) In silvering of mirrors and silver plating.

(iv) In the preparation of hair dyes and making indelible ink.

(v) Its 2% solution is used in medicine for granular eyelids, and for removing hair growth from skin.

14.7. Photography

The principle of photography was given by Niepce de sanint-victor about 1820. The photographic method was first realised by Daguerre in 1838. Now a days in ordinary photography, gelatin-silver bromide plates are used. It was introduced by Maddox in 1871. The principle is based on the sensitiveness of silver bromide or silver halide to the action of light. The mechanism of the changes which occur by the action of light on silver halides is not exactly known. Silver salts are photo sensitive.

Sensitised plates : In preparing plates, a soluble bromide or iodide or a mixture of bromide and iodide reacts with silver nitrate solution in presence of gelatin or collodion thus precipitating silver bromide or iodide on the plate.

$$NH_4Br+AgNO_3 \rightarrow AgBr+NH_4NO_3$$

This emulsion (mixture containing ammonium bromide, and silver nitrate in presence of gelatin) is kept in a warm room so that the particles of silver may grow in size. This process is known as ripening. The emulsion is applied to plates of transparent celluloid. The plates are loaded in a dark room, aided with red light. The plates are usually orthochromatic i.e. sensitive to all colours except red but can be made sensitive to all colours including red light by adding certain organic dyes to emulsions. Such films are known as panchromatic plates.

Exposure : The photographic plates are exposed for a very short time in a suitable camera, when an actual, invisible but inverted image of the object is obtained. This image is called letent image. On exposing the plate to light, the silver salt is photo-chemically affected in such a way that the exposed portion is rendered more easily reducible to metallic silver, and that, too, in proportion to the light exposed to probably, the light causes some structural change in the halides as shown below :

$$2AgBr \rightarrow Ag_2Br + Br$$

Developing : The exposed plate is then dipped in a solution of reducing agent e. g. pyrogallol, quinol etc. The reduction of metal occurs in the portions of the plate which were illuminated. The plate becomes darkest where the image has been most bright and vice-versa. The plate is now known as negative. This operation is carried out in a dark room aided with red light.

$$\underset{\text{Hydroquinone}}{C_6H_4(OH)_2} + 2AgBr \rightarrow C_6H_4O_2 + 2Ag + 2HBr.$$

Fixing : The developed plate is washed and placed in a solution of hypo (sodium thiosulphate). The solution of hypo reacts with unacte silver bromide and dissolves it. The negative image remains on the plate.

$$2AgBr + Na_2S_2O_3 \rightarrow Ag_2S_2O_3 + 2NaBr$$
$$Ag_2S_2O_3 + 3Na_2S_2O_3 \rightarrow 2Na_3[Ag(S_2O_3)_2]$$

The plate is treated with cold water to remove the hypo-completely and then dried in warm air. The process is carried out in a dark room aided with red light.

Printing : The principle of printing is as if taking a negative of the negative picture already taken, but this time not on a plate but on a paper. It is done by exposing a print paper to light through the negative and thus a positive picture on a paper is obtained. The printed paper is developed, rinsed with water and placed in a fixing bath. When fixed, it is washed well and dried.

Toning : The positive image thus obtained is of disagreeable colour. It is improved by dipping it in a solution of gold chloride. The silver grains of the image are replaced by gold.

$$HAuCl_4 + 3Ag \rightarrow HCl + AgCl + Au$$

14.8 Gold

Symbol—Au *Atomic No.* 79

Atomic weight—197·2

Electronic Configuration—$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^1$.

Occurrence :

Gold occurs both in free and combined state.

(**i**) **Native state** : It is generally found in free state because it is a noble ment. The two important sources being.

(a) *Quartz veins* : In this state, the fine particles of gold along with silver and platinum remain embeded.

(b) *Alluvial sands* : This is present in those rivers which passes over auriferous rocks.

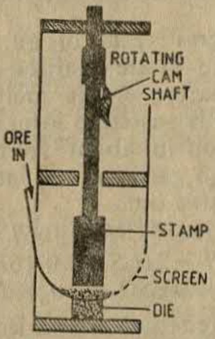
(**ii**) **Combined state** : Its compounds in nature are few. Bismuth aurite *AuBi*, *Calaverite* $AuTe_2$.

Extraction : Gold is extracted from quartz veins and alluvial sands by the following methods.

(i) Amalgamation process, (ii) Cyanide process, (iii) Chlorination process.

(**i**) **Amalgamation Process** : (a) *Stamp mill* : The chief and important source from which the metal is generally extracted is quartz veins.

The gold bearing quartz pieces are first broken into smaller ones in crushers and then powdered in a stamp mill. Each stamp mill consists of heavy Pestless (stamp) weighing 1250 1bs. which are raised by rotating camshaft. These fall at the rate of 100 times per minute into mortars (Die). The powdered ore is washed out of stamp mill by a current of water whereby fine particles pass out through the screens. These are worked up for the extraction of metal.



(b) *Amalgamation* : The finally powdered ore from the stamp mill is allowed to pass slowly over amalgamated copper plates. The gold combines with mercury to form an amalgam. This is scrapped off from the plates, squeezed to remove mercury and finally distilled. Mercury (b.p. 357°) distills over leaving free gold behind.

The process can remove 75-80% Gold, about 20% of gold is left unamalgamated in the residue called "Tailings".

(ii) Cyanide Process (Mac Arthur Forrest – 1887) : This is very good process for the removal of traces of gold from tailings of amalgamation process or from even poorer ores. It is based on the fact that gold dissolves in dilute solution (0·3%) of sodium cyanide in presence of atmospheric oxygen with the formation of complex cyanide.

$$4Au+8NaCN+2H_2O+O_2\rightarrow \underset{\text{Sod. aurocyanide}}{4Na[Au(CN)_2]}+4NaOH$$

or $$4Au+8CN^-+2H_2O+O_2\rightarrow 4[AuCN)_2]^{-1}+4OH^-$$

Alternative Method

The finely powdered ore from the stamp mill or tailings of amalgamation process is taken in large wooden vats provided with perforated false bottom covered with coconut mattings. It is then treated with 0·3% $NaCN$ solution in presence of excess of air for about 24 hours. The solution of sodium aurocyanide so obtained is treated with metal zinc when gold being less electro$+ve$ precipitated out.

$$2Na[Au(CN)_2]+Zn\rightarrow 2Au\downarrow+Na_2[Zn(CN)_4]$$

or $$[Au(CN)_2]^{-1}+Zn\rightarrow 2Au\downarrow+[Zn(CN)_4]^{-2}$$

The precipitated gold is treated with dil. H_2SO_4 to remove excess of zinc.

(iii) Chlorination Process : First of all Gold containing Pyrite ore is roasted then S and As are oxidised and volatilised. The ore becomes porous. The roasted ore is moistened with water in a trough then chlorine gas is passed to saturate the solution. Gold is converted to $AuCl_3$ solution in about 36 hours. The solution of $AuCl_3$ is removed and H_2S gas is passed into it or $FeSO_4$ solution is added. Gold is precipitated out.

$$2Au+Cl_2\rightarrow 2AuCl_3$$
$$2AuCl_3+2H_2S\rightarrow 2Au\downarrow 6HCl+3S$$
$$AuCl_3+3FeSO_4\rightarrow Au\downarrow+Fe_2(SO_4)_3$$

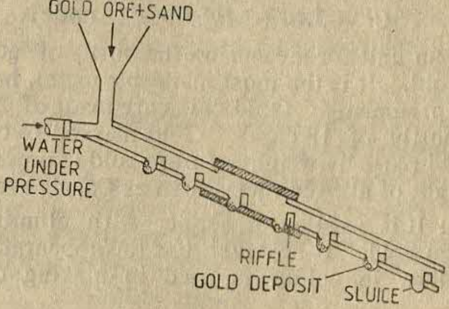
The precipitate is filtered out and dried. Gold is purified by fusion with borax.

Method adopted in Kolar Gold Field :

At Kolar Gold Fields there is combination of amalgamation and cyanide process for the isolation of gold. The gold bearing sands are crushed under heavy hammers and treated with excess of water. The mass is continuously stirred and allowed to flow over mercury coated copper plates to retain the metal as gold amalgam. The washing containing good amount of finely divided gold are subjected to cyanide Process.

Gold from Alluvial sands : The separation of gold from alluvial sand is based on the high specific gravity of Gold (19.3) compared with sand. Three different process are applied.

(i) *Panning* : The auriferous sand is mixed with water and given a rotary motion in a big iron pan. The heavier gold particles, settle down while the sand is washed away. It is the oldest method but is no longer employed.



(ii) *Placer mining* : In this case gold bearing sand is mixed with water and introduced into a sluice way system (as shown in fig). A powerful stream of water is passed through the channel which sweeps away the sand and the heavier gold collects on the bottom of the sluices.

(iii) *Hydraulic Mining* : It is employed when the gold bearing sand is found near the edge of a river. In this method, water under pressure is directed against the "earth" containing the gold. The "earth and gold are washed into the sluices as in placer mining.

Purification :

Gold obtained by any of the above process is impure and is purified by

(a) *Cupellation* : It is melted in presence of borax, silica and air in a cupel when impurities of *Pb*, *Cu* and *Zn* are oxidised and blown off. Silver is removed from gold chemically or electrolytically.

(b) *Parting or Quartation Process* : In this method silver is removed by treatment with conc. H_2SO_4. But a sample containing more than 30% gold or less than 70% silver is not attacked by acid of any strength and hence more silver is added to the fused metal till the percentage of gold is reduced to 25% (Quartation) or that of silver increased to 75% under these conditions silver dissolves out in conc. H_2SO_4 to form silver sulphate leaving behind pure gold.

Electrolytic Refining : This is usually followed for large scale refining and consists of

Cathode	..	Pure Gold
Anode	..	Impure gold
Electrolyte	..	$AuCl_3$ Sol. containing 10% HCl.

By using high current density, Gold is deposited on cathode while silver forms silver chloride and is precipitated. Other impurities also form chloride and are either precipitated or go into solution.

$$AuCl_3 \rightleftharpoons Au^{+++} + 3Cl^-$$
$$Au^{+++} + 3e \rightarrow Au \text{ (Cathode)}$$
$$3Cl^- + 3Au \rightarrow 3AuCl + 3e \text{ (Anode)}$$

Carat : It is an unit for measuring the purity of gold. 24 carat gold is a pure gold. It is the most malleable metal, hence it can not be used in gold ornaments. Gold coins are made of 22 carat gold, Jewellary is mostly of 18 carat. Gold marked 14 carat means an alloy in which 14 parts by weight of pure gold is present along with 10 parts by weight of alloyed metal such as Cu, Ag etc.

Rolled Gold : It is an alloy of copper with aluminium etc. but does not contain gold. It however, has the appearance of gold and being golden yellow in colour is used in making cheap type of oranaments.

Metals from a coin containing Au, Ag and Cu.

Since the coin contains a *very high percentage of gold* i.e. (65%) it is not attacked by dil. HNO_3, HCl etc. It is thus treated with aqua regia whereby all the three metals are converted into chlorides, ($AuCl_3$, $AgCl$, $CuCl_2$). Out of these, $AgCl$ being insoluble gets precipitated which is separated by filtration. It is then reduced to silver by fusion with Na_2CO_3 or reduced with nascent hydrogen evolved by zinc and dil. H_2SO_4.

$$HNO_3 + 3HCl \rightarrow NOCl + 2H_2O + 2\text{'}Cl\text{'}$$
$$Au + 3\text{'}Cl\text{'} \rightarrow AuCl_3$$
$$Ag + Cl \rightarrow AgCl\downarrow \text{ (white precipitate)}$$
$$Cu + 2Cl \rightarrow CuCl_2$$

(a) $$4AgCl + Na_2CO_3 \rightarrow 4NaCl + 4Ag + 2CO_2 + O_2$$

(b) $$Zn + H_2SO_4 \rightarrow ZnSO_4 + 2\text{'}H\text{'}$$
$$AgCl + H \rightarrow Ag + HCl$$

The filtrate containing $AuCl_3$ and $CuCl_2$ is treated with ferrous sulphate whereby gold chloride is reduced to gold which gets precipitated.

$$AuCl_3 + 3FeSO_4 \rightarrow Au\downarrow + Fe_2(SO_4)_3 + FeCl_3$$

It is filtered and the filtrate is treated with H_2S to get a black precipitate of copper sulphide. It is oxidised by conc. HNO_3 to get copper nitrate. This is treated with iron to get a precipitate of copper or is electrolysed to get copper at cathode.

$$CuS + 2HNO_3 \rightarrow Cu(NO_3)_2 + H_2S$$

Properties of Gold :

Physical : (i) It is a bright yellow metal. It melts at 1063°C and the moleten gold appears green.

(ii) Its density is 19·50 g. cm^{-2}.

(iii) It is extremely malleable and ductile.

(iv) Its thermal and electrical conductivities are very high.

(v) Gold occludes (absorbs) oxygen, hydrogen and carbon monoxide.

Chemical : (i) *Action of air* : Gold is a noble metal. Hence it remains unaffected by dry and moist air.

(ii) *Action of alkali* : Cyanide. Gold dissolves in sodium or potassium cyanide solution forming the complex dicyanoaurate (I) ion.

$$4Au+8CN^{-}+2H_2O+O_2\rightarrow4[Au(CN)_2]^{-1}+4OH^{-}$$

e.g. $4Au+8NaCN+2H_2O+O_2\rightarrow4Na[Au(CN)_2]+4NaOH$

Sod. aurocyanide

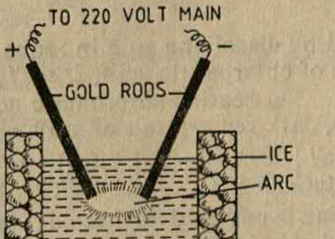
(iii) *Action of alkalies* : It does not react with alkalies.

(iv) *Action of Aqua Regia* : It dissolves in aqua regia (3 HCl : HNO_3 both conc.) producing chlorauric acid, $HAuCl_4$

$$HNO_3+3HCl\rightarrow2H_2O+NOCl+2\text{‘}Cl\text{’}[\times3]$$
$$Au+3Cl\rightarrow AuCl_3[\times2]$$
$$\underline{AuCl_3+HCl\rightarrow H[AuCl_4]}$$
$$3HNO_3+11HCl+2Au\rightarrow2H[AuCl_4]+6H_2O+3NOCl$$

Uses : (i) For making ornaments, (ii) For making coins, (iii) Gold salts are used in photography and in colouring glass.

Colloidal Gold : It is prepared (i) by striking an electric arc between two gold rods below the surface of water containing KOH and some protecting colloids.



(ii) by reduction of gold chloride solution with stannic and stannous chlorides.

The gold is precipitated along with colloided stannic acid.

$$2AuCl_3+3SnCl_2\rightleftharpoons2Au\downarrow3SnCl_4$$
$$SnCl_4+4H_2O\rightleftharpoons Sn(OH)_4\downarrow+4HCl$$

(iii) It can also be obtained by the reduction of Gold chloride with formaldehyde or hydrozine.

(iv) In case of reduction is carried out with $SnCl_2$, a colloidal gold having beautiful purple colour, "*Purple of cassius*" is obtained. It is used for colouring glass and enamels.

14.9 Compounds of Gold

Gold exhibits oxidation states of +1 (*aurous*) and +3 (*auric*).

$_{79}Au$	..	2, 8, 18, 32, 18, 1
Au	..	2, 8, 18, 32, 18 (aurous)
Au	..	2, 8, 18, 32, 16 (auric)

Compounds of gold are thermally unstable and yield the free metal on gentle heating. In solutions gold ions are present in the complexed form. In the aurous state the compounds are unstable and very disproportionate into auric compounds and metallic gold.

$$3Au \rightarrow 2Au + Au^{3+}$$

1. Aurous chloride, Gold (I) chloride, $AuCl$:

Preparation : It is obtained by heating pure auric chloride at 175°

$$AuCl_3 \rightarrow AuCl + Cl_2$$

Properties :

(i) It is yellow solid, sparingly soluble in water.

(ii) *Action of water* : It decomposes to form auric chloride.

$$3AuCl \rightarrow AuCl_3 + 2Au$$

(iii) *Action of chlorine* : It forms auric chloride.

$$AuCl + Cl_2 \rightarrow AuCl_3$$

(iv) *Action of NaOH* : It gives precipitate of aurous oxide.

$$2AuCl + 2NaOH \rightarrow Au_2O + 2NaCl + H_2O$$

2. Auric chloride, Gold III Chloride, $AuCl_3$

Preparation :

(i) It is prepared by dissolving gold in aqua regia when yellow needle like crystals of chloroauric acid, $HAuCl_4$ separate on concentrating the solution. On heating chloroauric acid in a current of dry chlorine at 200, dark red crystals of auric chloride are obtained.

$$2Au + 11HCl + 3HNO_3 \rightarrow 2H[AuCl_4] + 3NOCl + 6H_2O$$
$$H[AuCl_4].4H_2O \rightarrow AuCl_3 + HCl + 4H_2O.$$

(ii) When chlorine is passed over heated Gold metal at 150°C then anhydrous gold chloride is obtained.

$$2Au + 3Cl_2 \rightarrow 2AuCl_3$$

Properties :

(i) It is red crystalline solid, soluble in water and organic solvents.

(ii) *Action of heat* : It decomposes at 175°C to form aurous chloride.

$$AuCl_3 \rightarrow AuCl + Cl_2$$

(iii) *Action of HCl and KCl* : It forms chloroauric acid and its salt

$$AuCl_3 + HCl + H[AuCl_4]$$
$$AuCl_3 + KCl \rightarrow K[AuCl_4]$$

(iv) *Action of alkalies*: (MOH, $M = Na, K$)

When $NaOH$ solution is added to auric chloride solution then brown coloured precipitate of auric oxide is obtained.

$$\begin{array}{c}AuCl_3+3NaOH\rightarrow AuO.OH+3NaCl+H_2O[\times 2]\\ 2AuO\ OH\rightarrow Au_2O_3+H_2O\\ \hline 2AuCl_3+6NaOH\rightarrow Au_2O_3+6NaCl+3H_2O.\end{array}$$

(v) *Action of alkali Cyanide* (MCN $M=Na, K$)

It forms a complex sodium or potassium auricyanide.

$$AuCl_3+MCN\rightarrow M[Au(CN)_4]+3MCl$$

(vi) *Action of sodium thiosulphate* : When sodium thiosulphate solution is added to gold chloride solution then sodium auro thiosulphate solution is obtained.

$$AuCl_3+4Na_2S_2O_3\rightarrow \underset{\text{Sod. aurothiosulphate}}{Na_3[Au(S_2O_3)_2]}+Na_2S_4O_6+3NaCl$$

In this reaction $AuCl_3$ acts as an oxidising agent.

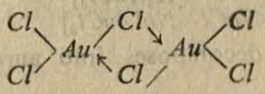
(vii) *Action of Ferrous sulphate* : When $FeSO_4$ solution is added to $AuCl_3$ then metallic gold is obtained. In this reaction $AuCl_3$ acts as an oxidising agent.

$$AuCl_3+3FeSO_4\rightarrow Au\downarrow+Fe_2(SO_4)_3+FeCl_3$$

(viii) *Action of Stannous chloride* : When $SnCl_2$ is added to $AuCl_3$ then metallic Au is obtained. In this reaction also $AuCl_3$ acts as an oxidising agent.

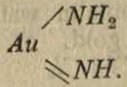
$$2AuCl_3+3SnCl_2\rightarrow 2Au+3SnCl_4.$$

Structure. The vapour-density of auric chloride shows that it exists as its dimer, Au_2Cl_6, which may be assigned the following structure.



Uses. (i) In photography for toning, (ii) As a specific antidote for snake poisoning.

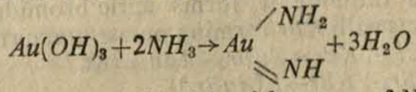
3. Fulminating Gold (Au)



$$Au\begin{array}{l}\diagup NH_2\\ \diagdown\!\!\diagdown NH.\end{array}$$

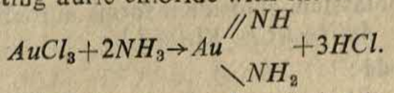
Preparation : It is prepared

(a) by the action of conc. NH_4OH on auric hydroxide.



$$Au(OH)_3+2NH_3\rightarrow Au\begin{array}{l}\diagup NH_2\\ \diagdown\!\!\diagdown NH\end{array}+3H_2O$$

(b) by treating auric chloride with excess of NH_3



$$AuCl_3+2NH_3\rightarrow Au\begin{array}{l}\diagup\!\!\diagup NH\\ \diagdown NH_2\end{array}+3HCl.$$

It is an olive green powder and explode when heated or struck. It dissolves in boiling KCN solution forming Potassium tetracyanoaurate, $K[Au(CN)_4]$.

4. Purple of Cassius.

It is the most important and widely used form of colloidal gold, discovered by Cassius in 1865. It is obtained by mixing stannous chloride solution with a dilute solution of gold chloride.

$$3SnCl_2+2AuCl_3 \rightleftharpoons 2Au\downarrow+3SnCl_4$$
$$SnCl_4+4H_2O \rightleftharpoons Sn(OH)\downarrow+4HCl$$

A colloidal precipitate of stannic acid absorbs colloidal particles of gold which has a beautiful purple colour and is known as "Purple of Cassius". The atannic acid also acts as a protective colloid. It may be considered as a solid solution of gold in stannic acid.

It is used in colouring glass and pottery.

5. Chlorides :

Auric Chloride, $AuCl_3$. When gold is dissolved in aqua regia and the solution is evaporated, yellow crystals of chloroauric acid, $HAuCl_4\ 2H_2O$ with water. It is a non-polar compound like alcohol and ether.

$$HAuCl_4 \rightarrow AuCl_3+HCl$$

On exposure to sunlight or on heating it decomposes into aurous chloride and chlorine.

$$2AuCl_3 \rightarrow AuCl+Cl_2$$
$$2AuCl \rightarrow 2Au+Cl_2$$

With hydrochloric acid it forms chloroauric acid and with alkali chlorides it forms well defined crystalline salts.

$$AuCl_3+HCl \rightarrow H[AuCl_4]$$
$$AuCl_3+NaCl \rightarrow Na[AuCl_4]$$

Its aqueous solution decomposes into aurous chloride and hydrogen peroxide.

$$AuCl_3+2H_2O \rightarrow AuCl+H_2O_2+2HCl.$$

Aurous chloride, AuCl

It is formed when auric chloride is heated to 175°C. It is a yellow solid, solid, sparingly soluble in water and heating decomposes to form auric chloride and gold.

$$AuCl_3 \rightarrow AuCl+Cl_2$$

It is oxidised by chlorine to auric chloride.

$$AuCl+Cl_2 \rightarrow AuCl_3$$

With potassium bromide it forms auric bromide and metallic gold, the forms reacts with *KBr* forming potassium auribromide.

$$3AuCl+3KBr \rightarrow AuBr_3+2Au+3KCl$$
$$AuBr_3+KBr \rightarrow K[AuBr_4]$$

With sodium or potassium chloride it forms aurochloride.

$$AuCl+KCl \rightarrow K[AuCl_4]$$

Analytical Test for Gold :

On adding boiling solution of gold or its salts into concentrated solution of stannous chloride, a purple colour in the precipitated stannous hydroxide is obtained. It is a very sensitive test for gold.

QUESTIONS

Long Type Questions

1. Discuss the position of the coinage metals in the periodic table. In what respects do these elements and their compounds resemble one another ? [M. U 1967 A, '71 A]

2. Name the important naturally occuring compounds of copper and describe a method for the extraction and refining of copper from its sulphide ores. Mention the chief uses of the metal. [Bhag. U. 1968 A; P. U. '70 A; B. U. '68 A; R. U. '79 A; M. U. '78 A]

3. What happens when copper is (a) heated in air, (b) heated in steam, (c) treated with HCl, (d) HNO_3 and (e) H_2SO_4.

4. What are the chief sources of silver ? Describe a method for the extraction of silver from its ores. State the uses of silver. [P. U. 1968 A; M. U. '76 A, '81 A]

5. Describe the methods of extraction of silver from argentiferrous lead, indicating the principles involved. [P. U. 1964 A; M. U. '65 A; B. U. '66 A]

6. (a) How would you recover silver from silver wire ? [M. U. 1967 A]
   (b) How would you prove that bazar silver contains silver and copper ? How would you obtain a pure silver from bazar silver. [P. U. 1961 A; M. U. '76 A]
   (c) How would you obtain pure sample of silver from a silver coin ? [M. U. 1967 A]

7. What happens when silver chloride reacts with :
   (i) Ammonia [P. U. 1975 A; M. U. '74 S]
   (ii) Potassium cyanide [M. U. 1970 A; P. U. '75 A]
   (iii) Hypo [M. U. 1974 S; P. U. '75 A]
   (iv) Nascent hydrogen [M. U. 1974 S]
   (v) Na_2CO_3 (vi) $NaCH$

8. How does gold occur in nature ? Describe the process used for the extraction of the metal and its purification. How would you assay a sample of alluvial gold ore ? [P. U. 1970 A; M. U. & I. A; B. U. '66 A]

9. How is gold extracted from gold bearing rocks ? Give the chemical reactions in the method employed. State the uses of gold. [P. U. 1968 A, '82 S; B. U. '62 A. '71 A]

10. How would you prepare a sample of pure gold from an alloy of copper and gold ? Write short note on gold plating. [P. U. 1970 A]

Short Type Questions

11. What happens when copper sulphate solution reacts with :
    (a) NH_4OH, (b) KI, (c) KCN, (d) Zn, (e) KOH, (f) SO_2.

12. Write notes on :
    (a) Alloys of copper (b) Blue vitriol
    (c) Lunar caustic [P. U. 1982 S] (d) Purple of Cassius

(e) Colloidal Gold (f) Carat
(g) Photography (h) Fulminating gold.
[P. U. 1970 A; M. U. '71 A, '80 A]

13. How would you prepare specimens of :
(a) Cuprous chloride. (b) Cuprous oxide
(c) Cupric oxide, (d) Crystals of copper sulphate starting from copper ?

[HINT : (a)
$$\begin{tikzcd} Cu \arrow[r, "HNO_3"] & Cu(NO_3)_2 \arrow[r, "\text{heat}"] & CuO \arrow[r, "HCl"] & CuCl_2 \arrow[d, "Cu"] \\ & & & CuCl. \end{tikzcd}$$

(b) $Cu \xrightarrow{H_2SO_4} CuSO_4 \xrightarrow{NaOH} Cu(OH)_2 \xrightarrow{\text{heat}} CuO \xrightarrow{\text{Reduction}} Cu_2O.$
(c) as (a)
(d) as (b)

14. Give the reactions of silver with the following—
(a) halogens, (b) acids, (c) alkalies (d) Sodium cyanide.

15. How would you recover silver from Photographic fixing baths ?

[HINT :
$$\begin{tikzcd} & 2AgBr+3Na_2S_2O_3 \arrow[r] & Na_4[Ag_2(S_2O_3)_3]+2NaBr. \arrow[d, "NaCN"', "\text{boil}"] \\ Ag\downarrow+Na_2[Zn[CN_4] & Na[Ag(CN)_2] \arrow[l, "Zn"'] & Ag_2S\downarrow \arrow[l] \end{tikzcd}$$

16. What reactions take place when a solution of silver nitrate is added to solution of (a) Sodium thiosulphate and (b) Sodium hydroxide.
[P. U. 1970 A; R. U. '71 A; M. U. '70 A]

17. Write a short note on gold plating.

18. What happens when auric chloride solution is treated with (a) ammonia (b) stannous chloride.

19. Give the action of the following on Gold :
(a) Acid, (b) Base, (c) Halogens, (d) Sodium Cyanide.

20. Fill up the blank and balance.
(i) $AgCl+KCN \longrightarrow KCl+\ldots\ldots$ [IIT 1968]
(ii) $AgCl+Na_2S_2O_3 \longrightarrow$ [IIT 1972]
(iii) $CuSO_4+KCN \longrightarrow$ [IIT 1972]
(iv) $CuSO_4+NH_4OH$ (excess) $\longrightarrow$ [B. C. E. 1984]
(v) $AuCl_3+SnCl_2 \longrightarrow$ [IIT 1978]

21. In column A, the formulae of the compounds are given and in B their trade names are given—Match A with B.

A	B
1. $CuSO_4\,5H_2O$	(a) Horn silver
2. $Cu(OH)_2\,Cu(CH_3COO)_2$	(b) Lunar caustic
3. $AgNO_3$	(c) Fulminating Gold
4. $AgCl$	(d) Malachite
5. $Na_2S_2O_3\,5H_2O$	(e) Verdigiris
6. Au	(f) Blue vitriol
7. $CuCO_3\,Cu(OH)_2$	(g) Hypo

22. **Fill up the blank** (one choice from bracket)
(a) Blue vitriol is.........in nature (acidic/basic, neutral)
(b) $AgCl$ is known as......... (hypo, lunar caustic, Horn silver)
(c) $Ag_2S.Sb_2S_3$ is known as...... (ruby silver, Argentiferrous lead, malachit)
(d) Cu_2O is......... in colour (Red, Blue, green)

Select and write correct answer for the following :

23. Lunar caustic is :
(1) $AgCl$ (2) $NaOH$ (3) $AgNO_3$ (4) $AgBr$.

24. Which of the following ion is obtained when excess of NH_4OH is added to $CuSO_4$ solution ?
(1) $Cu(OH)_2$ (2) $[Cu(NH_3)_4]SO_4$
(3) $[Cu(NH_3)_4]^+$ (4) $[Cu(NH_3)_4]^{++}$.

25. When excess of KCN is added to $AgCl$ then the complex formed is
(1) anionic (2) cationic (3) neutral (4) None.

26. Which of the following is an ore of copper ?
(1) Horn silver (2) Lunar caustic (3) Azurite (4) Phosphorite.

27. Which one of the following properties would you not expect copper (Cu) to exhibit ?
(1) High thermal conductivity (2) Low electrical conductivity (3) Ductilibity (4) Malleability. [N.C.E.R.T. 1975]

28. Parke's Process is used in the extraction of :
(1) Iron (2) Zinc (3) Silver (4) Sodium. [B.H.U. 1977]

29. Black sulphide is formed by the action of H_2S on :
(1) cadmium chloride (2) cupric chloride
(3) Zinc chloride (4) Sodium chloride. [I.I.T. 1978]

30. Extraction of silver from commercial lead is possible by :
(1) Mond's process (2) Parke's process
(3) Haber's process (4) Clark's process. [B. H. U. 1979]

31. $AgCl$ on fusion with Na_2CO_3 gives
(1) Ag_2CO_3 (2) Ag_2O (3) Ag (4) Silver carbide. [CPMT 1980]

32. Which of the following pairs constitute brass.
(1) Zinc and copper (2) Sn and Cu
(3) Ni and Cu (4) Ni and Zn. (B.C.E. Test 1980]

□□□

CHAPTER 15

STUDY OF GROUP II-A ELEMENTS IN PERIODIC TABLE

Periodic Discussion :

The elements of group II of the periodic table are :

$$\begin{tikzcd}[column sep=small] & & Ca-Sr-Ba-Ra & \text{.. II-A} \\ Be-Mg \arrow[urr, no head] \arrow[drr, no head] & & & \\ & & Zn-Cd-Hg & \text{.. II-B} \end{tikzcd}$$

The sub-group A consists of the normal elements *Be*, *Mg*, *Ca*, *Sr*, *Ba*, and *Ra* and the sub-group B of the transitional elements *Zn*, *Cd*, and *Hg*. Their electronic arrangements are given below :

II-A

${}_{4}Be = 2, 2$ or $1s^2, 2s^2$

${}_{12}Mg = 2, 8, 2$ or $1s^2, 2s^2 2p^6, 3s^2$

${}_{20}Ca = 2, 8, 8, 2$ or $1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2$

${}_{38}Sr = 2, 8, 18, 8, 2$ or $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6, 5s^2$

${}_{56}Ba = 2, 8, 18, 18, 8, 2$ or $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}, 5s^2 5p^6, 6s^2$

${}_{88}Ra = 2, 8, 18, 32, 18, 8, 2$ or $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^{14}, 5s^2 5p^6 5d^{10}, 6s^2 6p^6, 7s^2$

II-B

${}_{30}Zn = 2, 8, 18, 2$ or $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2$

${}_{48}Cd = 2, 8, 18, 18, 2$ or $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}, 5s^2$

${}_{80}Hg = 2, 8, 18, 32, 18, 2$ or $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^{14}, 5s^2 5p^6 5d^{10}, 6s^2$.

They are all characterised by their having two valency electrons. The **penultimate orbit** of II-A group elements contains 8 **electrons** while those of II-B group elements contain 18 **electrons**. Thus, the **Kernel** of II-A group elements is similar to an inert gas preceding the element.

In some properties *Be* and *Mg* differ from the other elements of II-A and resemble those of II-B. For this reason, formerly these elements were included in II-B but after the fundamental difference in atomic structure was recognised, they have been included in II-A.

The term **alkaline earth metals** was formerly used only for calcium, strontium and barium but now it has been extended to all the elements of II-A. These elements are placed in *s*-block while elements of II-B are placed in *d*-Block.

Alkaline Earths :

Usually, Calcium, Strontium and Barium are known as **alkaline earths**. These elements are placed in the sub-group-A of the second group of the periodic table with Beryllium, Magnesium and Radium. Their inclusion in the same group of the periodic table may be justified as they show a marked resemblance and regular gradation in their properties as the atomic weight increases.

Resemblances :

(i) *Physical state* : They are all soft, silvery white and low melting metals.

(ii) *Occurrence* : They do not occur in free state in nature.

(iii) *Extraction* : All are extracted by the electrolysis of their fused chlorides.

(iv) *Colour to the flame* : Excepting *Be* and *Mg* all impart characteristic colour to the flame.

Ca—brick red; *Sr*—crimson; *Ba*—apple green; *Ra*—red.

(v) *Electronic arrangement* :

$Be_4 \rightarrow 2, 2$	$\boxed{He}$	$2s^2$
$Mg_{12} \rightarrow 2, 8, 2$	$\boxed{Ne}$	$3s^2$
$Ca_{20} \rightarrow 2, 8, 8, 2$	$\boxed{Ar}$	$4s^2$
$Sr_{38} \rightarrow 2, 8, 18, 8, 2$	$\boxed{Kr}$	$5s^2$
$Ba_{56} \rightarrow 2, 8, 18, 18, 8, 2$	$\boxed{Xe}$	$6s^2$
$Ra_{88} \rightarrow 2, 8, 18, 32, 18, 8, 2$	$\boxed{Rn}$	$7s^2$

All contain 2 valency electrons. The core of all these metals is similar to that of inert gas preceding the elements. All of them are **normal elements**.

(vi) *Electropositive character* : All of them are strongly electropositive, divalent and chemically active elements.

(vii) *Action of air* : Easily tarnished in air forming a film of oxide, hydroxide and carbonate, *Ra* forms thin film of the black nitride.

When heated in oxygen form oxides of the type *RO*, excepting *Ba* and *Ra* which form peroxides.

$$2Ca+O_2 \rightarrow 2CaO$$

(viii) *Action of water* : All react with water, though under different conditions to form the hydroxide with the evolution of hydrogen. *Be* is the least active with water while *Ba* is most active.

(ix) *Action of acids :* All react with acids forming salts and evolving hydrogen.

(x) *Action of non-metals* : On heating with *H*, *N*, *Cl*, *C* and *S* all form hydrides, nitrides, chlorides, carbides and sulphides.

$$Ca+H_2 \rightarrow CaH_2$$
$$3Ca+N_2 \rightarrow Ca_3N_2$$
$$Ca+Cl_2 \rightarrow CaCl_2$$
$$Ca+2C \rightarrow CaC_2$$
$$Ca+S \rightarrow CaS$$

Their nitrides decompose water evolving NH_3.

$$Ca_3N_2+6H_2O \rightarrow 3Ca(OH)_2+2NH_3$$

(xi) *Action of* NH_3 : They dissolve in liq. NH_3 and on evaporating they form hexa-ammoniates $M(NH_3)_6$. *M* is II-A group element.

(xii) Salts of alkaline earth metals are highly hyd rated e.g.

$$MgCl_2.6H_2O;\ CaCl_2.6H_2O$$

Generalities of their salts :

(i) *Chlorides* : They are soluble in water and crystallize from aqueous solutions in the form of hydrates containing varying number of molecules of water of crystallization.

(ii) *Sulphates* : They are insoluble in water except $CaSO_4$ which is sufficiently soluble in water. Solubility decreases with increase in atomic weight of metal.

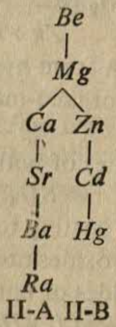
(iii) *Chromates* : *Ca* and *Sr* chromates are soluble in acetic acid while barium chromate is insoluble. Solubility decreases with increase in atomic weight.

(iv) *Oxides* : They react with water forming hydroxides.

Magnesium as Bridge Element :

The II group of Mendeleeff's periodic table consists of 9 elements of which *Be* and *Mg* are the typical elements. The branching of the II group begins at *Mg* to give two sub-groups

II-A..(*Ca*, *Sr*, *Ba*, *Ra*)
II-B..(*Zn*, *Cd*, *Hg*)



and thus it is regarded as bridge element.

The position of *Mg* is justified by the study of electropositive character. It increases from *Be* to *Ra* and decreases from *Be* to *Hg* as the atomic weight increases. In other words, *Ra* is most electropositive and *Hg* is the least in II group so that *Mg* is in between *Ca* and *Zn*.

It is thus expected that *Mg* should resemble both the sub-groups which is actually shown by its close similarity with calcium as well as zinc.

Magnesium resembles Calcium :

(i) Both have similar electronic structure.

(ii) Both are light, malleable and ductile.

$$Mg_{12}=2, 8, 2; \qquad Ca_{20}=2, 8, 8, 2$$

(iii) With dil. HNO_3, both give H_2 gas.

$$Mg+2HNO_3\rightarrow Mg(NO_3)_2+H_2\uparrow$$
$$Ca+2HNO_3\rightarrow Ca(NO_3)_2+H_2\uparrow$$

(iv) They form nitrides when heated with N_2,

$$3Mg+N_2\rightarrow Mg_3N_2$$
$$3Ca+N_2\rightarrow Ca_3N_2$$

(v) They form oxides which are basic and stable to heat.

(vi) They form soluble sulphides.

(vii) They do not form complex salts.

Magnesium resembles Zinc :

(i) They do not impart colour to flame.

(ii) They are not tarnished by dry air.

(iii) They do not decompose cold water. They decompose steam to form oxide and H_2 gas.

$$Zn + H_2O \rightarrow ZnO + H_2$$

(iv) They do not form hydrides.

(v) They form organo-metallic compounds e.g.

$$R-Mg-X \text{ and } R-Zn-X.$$

(vi) The sulphates of both metals are isomorphous (Epsom Salt $MgSO_4.7H_2O$. White vitriol $ZnSO_4.7H_2O$) and decompose on heating to give their oxides.

(vii) Their hydroxides are insoluble in water.

(viii) The chlorides of both are hydrolysed by water.

$$ZnCl_2 + H_2O \rightarrow Zn(OH)Cl + HCl$$

$$MgCl_2 + H_2O \rightarrow Mg(OH)Cl + HCl$$

Magnesium

At. No. 12. *At. Mass* = 24.

Electronic configuration : $1s^2, 2s^2\ 2p^6, 3s^2$.

History : The compound known as epsom salt (Magnesium sulphate) was isolated from spring water in Epsom (England) in 1795. Davy isolated the metal in the impure state in 1809 electrolytically and called it "Magnium" which was later changed to Magnesium.

Occurence : It does not occur free in nature but its compounds are widely distributed. Its important minerals are :

(i) Magnesite, $MgCO_3$, (ii) Dolomite, $MgCO_3.CaCO_3$, (iii) Carnallite, $KCl.MgCl_2.6H_2O$, (iv) Asbestos, $CaMg_3(SiO_3)_4$.

Extraction : It is extracted by

1. Modern Electrolytic method, 2. Electrolysis of MgO, 3. Reduction of MgO, 4. Sea water.

Modern Electrolytic Method : **1. From Fused $MgCl_2$:** Magnesium is obtained by the electrolysis of fused $MgCl_2$ but the process is met with the following difficulties—

(i) Fusion temperature of $MgCl_2$ is quite high.

(ii) It is not good conductor of electricity.

(iii) $MgCl_2$ may be hydrolysed by water present in carnallite to form magnesium hydroxy chloride.

$$MgCl_2+H_2O \rightleftharpoons Mg(OH)Cl+HCl$$

(iv) On electrolysis of $MgCl_2$, Mg metal liberated at cathode may come in contact with chlorine which is liberated at anode.

(v) O_2 and N_2 of the air present in the vessel may react with molten metal.

To overcome the above difficulties :

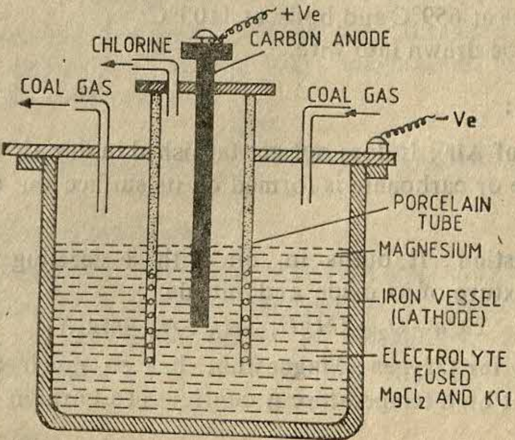
(a) The electrolyte used is fused $MgCl_2$ to which some $NaCl$ has also been added. The later reduces the melting point, increases the conductivity of the electrolyte and prevents the hydrolysis of magnesium chloride.

(b) The air of the apparatus is displaced by an inert gas such as coal gas or hydrogen.

(c) The electrolysis is carried out in iron cell which acts as cathode. A graphite anode is surrounded by a porcelain hood to escape chlorine.

On electrolysis magnesium is liberated and being lighter floats on the surface of the electrolyte and is drawn off. It is about 92·0% pure.

2. From Fused Magnesium Chloride by Electrolysis : Magnesium is also obtained by the electrolysis of magnesium chloride dissolved in fused mixture of magnesium, potassium and sodium chlorides at 950°C. Magnesium is liberated at cathode while chlorine is evolved at anode.



3. From Magnesium Oxide by Reduction : Large amount of magnesium is obtained in U. S. A. by the reduction of magnesium oxide with carbon at 2000°C on electric arc.

$$MgO + C \rightarrow Mg + CO \uparrow$$

The reaction is reversible and endothermic and thus the gaseous products (magnesium vapour and CO gas) are immediately cooled to about 200°C to prevent the redistillation in vacuum.

4. Magnesium from Sea water : (Dows process) : Sea water contains about 13% Mg and is worked up as below :

(i) Sea water is filtered and heated with slaked lime to precipitate magnesium as hydroxide.

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2$$

(ii) The ppt. of $Mg(OH)_2$ is dissolved in HCl to get magnesium chloride which on concentration and cooling yields $MgCl_2.6H_2O$.

(iii) It is heated to dehydrate until it is hemihydrate ($MgCl_2.2H_2O$). It is only after this stage that it gets hydrolysed on further heating.

(iv) This is fused and electrolysed as in method (1). Mg is extracted by this method in Louisiana and Texas (U. S. A.)

Properties of Magnesium

Physical :

1. Magnesium is silver white, lustrous, ductile, and malleable metal.
2. It is a light metal, specific gravity being 1·74.
3. It melts at 659°C and boils at 1100°C.
4. It can be drawn into wire.

Chemical :

1 Action of Air : It does not get tarnished in dry air but a white film of oxide or carbonate is formed on its surface on exposure to moist air.

2. Combustion : It burns in air with a dazzling white light forming a mixture of its oxide and nitride.

$$2Mg + O_2 \rightarrow 2MgO; \; 3Mg + N_2 \rightarrow Mg_3N_2$$

3. Affinity for Oxygen : Magnesium has so much affinity with oxygen that at high temperature it continues to burn in CO_2, SiO_2, B_2O_3 etc.

$$2Mg + CO_2 \rightarrow 2MgO + C;\ 2Mg + SiO_2 \rightarrow 2MgO + Si$$
$$3Mg + B_2O_3 \rightarrow 3MgO + 2B$$

4. Action of Water : At room temperature, water has no action on the metal, it decomposes boiling water slowly but burns brilliantly if heated in steam forming its oxide and hydrogen.

$$Mg + H_2O \rightarrow MgO + H_2 \uparrow$$

5. Action of Alkalies : Magnesium does not act upon alkalies.

6. Action of Acids : (a) With dilute H_2SO_4, it liberates hydrogen while with hot and concentrated acids sulphur dioxide is evolved.

$$Mg + H_2SO_4 \rightarrow MgSO_4 + H_2 \uparrow$$
$$Mg + 2H_2SO_4 \rightarrow MgSO_4 + SO_2 \uparrow + 2H_2O$$

(b) With dilute or conc. HCl, magnesium liberates hydrogen.

$$Mg + 2HCl \rightarrow MgCl_2 + H_2 \uparrow$$

(c) Cold and dilute nitric acid reacts with magnesium to evolve hydrogen.

$$Mg + 2HNO_3 \rightarrow Mg(NO_3)_2 + H_2 \uparrow$$

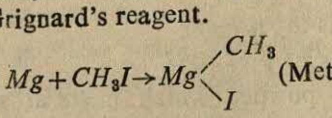
(d) With very dilute nitric acid the reaction is vigorous and ammonia is evolved which reacts with nitric acid to yield ammonium nitrate.

$$\begin{array}{l} Mg + 2HNO_3 \rightarrow Mg(NO_3)_2 + 2\text{'}H\text{'}\ [\times 4] \\ \underline{2HNO_3 + 8H \rightarrow NH_4NO_3 + 3H_2O\qquad\qquad} \\ 4Mg + 10HNO_3 \rightarrow NH_4NO_3 + 4Mg(NO_3)_2 + 3H_2O \end{array}$$

7. Displacement of Metals : Being strong electropositive, it displaces nearly all the metals from the solutions of their salts e.g.

$$Mg + 2AgNO_3 \rightarrow 2Ag \downarrow + Mg(NO_3)_2$$

8. Formation of Grignard's Reagent : Mg dissolves in dry etheral solution of alkylhalides forming alkyl magnesium halide. This is known as Grignard's reagent.



$$Mg + CH_3I \rightarrow Mg\begin{array}{l} \diagup CH_3 \\ \diagdown I \end{array}$$

(Methyl Magnesium iodide)

Uses : Magnesium is used :

(i) in pyrotechnics, fireworks, surgical flames, and in flash light in photography, (ii) as a reducing agent in the extraction of boron and silicon, (iii) as a de-oxidiser in metallurgy, (iv) in making Grignard's reagent which is a valuable tool in the synthesis of a large number of compounds in organic chemistry, (v) for producing vacuum in radio tubes.

Alloys of Magnesium

Alloy	*Composition*	*Uses*
1. Magnalium	$Al = 90\%$, $Mg = 10\%$	Scientific instruments, castings.
2. Duraluminium	$Al = 92\%$, $Cu = 4\%$, $Mg = 4\%$	Aeroplane and dirigible construction.
3. Dow metal	$Mg = 89\%$, $Al = 9\%$, $Zn = 2\%$	Light machinery.
4. Electron metal	$Mg = 95\%$, $Zn = 4{\cdot}5\%$, $Cu = 0{\cdot}5\%$	In the construction of air crafts.

Compounds of Magnesium

Magnesium Hydride, MgH_2 : It is prepared by passing hydrogen under pressure on heated magnesium powder.

$$Mg + H_2 \rightarrow MgH_2$$

It is light grey solid. Like other hydrides it gives out hydrogen when treated with water.

$$MgH_2 + 2H_2O \rightarrow Mg(OH)_2 + 2H_2 \uparrow$$

It is fairly stable and decomposes only when strongly heated.

Magnesium Oxide, MgO : It is formed when magnesite is heated to a high temperature

$$MgCO_3 \rightarrow 2MgO + CO_2 \uparrow$$

or when magnesium burns in oxygen.

$$2Mg + O_2 \rightarrow 2MgO$$

Properties : It is a white powder which melts at such a high temperature as 2300°C. It sets in water to give a firm mass. It is a basic oxide and dissolves in acids to give magnesium salts. In water it changes gradually to magnesium hydroxide.

$$MgO + H_2O \rightarrow Mg(OH)_2$$

Uses : (a) It is largely used as refractory material in furnaces. (b) It also finds application in medicine to lower the acidity of the stomach.

Magnesium Hydroxide, $Mg(OH)_2$:

Preparation : It is prepared by the addition of an alkali to the solution of a magnesium salt.

$$MgSO_4 + 2NaOH \rightarrow Mg(OH)_2 \downarrow + Na_2SO_4$$

It is also precipitated by the addition of ammonium hydroxide in the presence of ammonium chloride. This fact helps in the separation of magnesium from iron, aluminium and chromium.

It is a weak base. When heated to a high temperature it gives MgO.

$$Mg(OH)_2 \rightarrow MgO + H_2O$$

Magnesium Carbonate, $MgCO_3$:

Preparation : (i) If sodium bicarbonate is added to a hot solution of a magnesium salt, magnesium carbonate is precipitated.

$$MgSO_4 + 2NaHCO_3 \rightarrow MgCO_3 \downarrow + Na_2SO_4 + CO_2 + H_2O$$

(ii) It is formed by heating magnesium bicarbonate.

$$Mg(HCO_3)_2 \rightarrow MgCO_3 + H_2O + CO_2 \uparrow$$

Properties : 1. It is a white powder insoluble in water.

2. On heating or on treatment with acids it evolves CO_2.

$$MgCO_3 \rightarrow MgO + CO_2 \uparrow$$

3. It is converted to $Mg(HCO_3)_2$ when CO_2 is passed into suspension of $MgCO_3$ in water.

$$MgCO_3 + H_2O + CO_2 \rightarrow Mg(HCO_3)_2$$

4. It reacts with acids to form salt, CO_2 and water.

$$MgCO_3 + 2HCl \rightarrow MgCl_2 + CO_2 \uparrow + H_2O$$
$$MgCO_3 + H_2SO_4 \rightarrow MgSO_4 + CO_2 \uparrow + H_2O$$

Uses : It is used :

1. as a refractory material, 2. in medicine as anti-acid laxative, 3. in tooth powder, cosmetics, silver polishes etc., 4. in rubber industry, 5. in vitreous precelain and fire resisting parts.

Magnesium Chloride, $MgCl_2.6H_2O$:

It occurs in sea water, some springs and in the mineral carnallite, $KCl.MgCl_2.6H_2O$.

Preparation : 1. It is prepared in the laboratory by dissolving the metal or its oxide, hydroxide, or carbonate in dilute hydrochloric acid and evaporating the solution to crystallize out $MgCl_2.6H_2O$.

$$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$$
$$MgCO_3 + 2HCl \rightarrow MgCl_2 + H_2O + CO_2 \uparrow$$

2. On large scale it is prepared from the mineral carnallite by fractional distillation. The mineral is fused and cooled to 175°C whereby less soluble KCl separates out as solid mass leaving $MgCl_2$ in the fused state. The fused mass is separated and further cooled when the remaining KCl crystallizes out. The fused mass is separated, cooled when $MgCl_2\ 6H_2O$ crystallises out.

1. **Properties** : It is a colourless, crystalline, solid extremely soluble in water. It has a bitter taste.

2. **Action of Heat** : On heating, the salt is dehydrated to the extent of dihydrate. On further heating it undergoes hydrolysis.

$$2MgCl_2.6H_2O \rightarrow Mg_2OCl_2 + 2HCl + 11H_2O$$
$$2Mg_2OCl_2 + O_2 \rightarrow 4MgO + 2Cl_2 + O_2$$

3. A concentrated solution of $MgCl_2$ when mixed with MgO forms a thick paste of $MgCl_2.5MgO.H_2O$ known as *Sorel's cement.*

Anhydrous Magnesium Chloride, $MgCl_2$:

Preparation : (i) It is obtained when dry chlorine or dry HCl gas is passed over red hot Magnesium.

$$Mg + Cl_2 \rightarrow MgCl_2$$
$$Mg + 2HCl \rightarrow MgCl_2 + H_2 \uparrow$$

(ii) Anhydrous chloride is also obtained by heating magnesium ammonium chloride.

$$NH_4Cl.MgCl_2.6H_2O \rightarrow MgCl_2.NH_4Cl.H_2O + 5H_2O$$
$$MgCl_2.NH_4Cl.H_2O \rightarrow MgCl_2 + NH_3 + HCl + H_2O$$

Properties : 1. It is a colourless, crystalline, deliquescent solid extremely soluble in water. It has bitter taste.

2. It forms compound $MgCl_2.6C_2H_5OH$ with ethyl alcohol.

Uses : 1. In the formation of Sorel's cement and in dental fillings.

2. In the preparation of artificial stones.

3. In cementing glass and metal together, and as a finish for plates as it takes up very good polish.

Magnesium Nitrate, $Mg(NO_3)_2.6H_2O$:

Preparation : (i) It is prepared by the action of dilute nitric acid on magnesium oxide, magnesium hydroxide, magnesium carbonate etc. and evaporating the solution to crystallization.

(a) $MgO+2HNO_3 \rightarrow Mg(NO_3)_2+H_2O$

(b) $Mg(OH)_2+2HNO_3 \rightarrow Mg(NO_3)_2+2H_2O$.

Properties : (i) It is a colourless, deliquescent substance, soluble in water and alcohol.

(ii) It decomposes on heating.

$$2Mg(NO_3)_2 \rightarrow 2MgO+4NO_2+O_2$$

Magnesium Sulphate ($MgSO_4.7H_2O$) or Epsom salt :

It occurs in nature as the mineral *Kieserite* $MgSO_4.7H_2O$ and *Epsomite* $MgSO_4.H_2O$ and also in some springs and river and well water. These are rich deposits of Kieserite in the *Stassfurt* salt beds.

Preparation : (i) It may be prepared by heating magnesium metal, its oxide, or carbonate with dil. H_2SO_4.

(a) $Mg+H_2SO_4 \rightarrow MgSO_4+H_2\uparrow$

(b) $MgO+H_2SO_4 \rightarrow MgSO_4+H_2O$

On evaporating the solution, magnesium sulphate is crystallized out.

(ii) It is obtained on commercial scale from kieserite, which is soluble with great difficulties. When placed in contact with water, it slowly hydrates itself and sets as a solid mass of epsomite, $MgSO_4.7H_2O$. This is recrystallized and sold as Epsom salt.

$$\underset{\text{Kieserite}}{MgSO_4.H_2O}+6H_2O \rightarrow \underset{\text{Epsomite}}{MgSO_4.7H_2O}$$

1. **Properties :** It is a white crystalline, deliquescent solid. It is soluble in water. It forms a number of hydrates containing 7, 6, 5, 2 and 1 molecule of water.

2. **Action of Heat :** On heating to 200°C it becomes anhydrous. On further heating it decomposes to form the oxide, MgO.

$$MgSO_4.7H_2O \xrightarrow{150°C} MgSO_4.H_2O+6H_2O$$

$$MgSO_4.H_3O \xrightarrow{200°C} MgSO_4+H_2O$$

$$\downarrow 800°C$$

$$MgO+SO_3$$

3. It is isomorphous with white vitriol, $ZnSO_4.7H_2O$.

4. It forms double salts with alkali metal sulphate e.g. $K_2SO_4\,MgSO_4.6H_2O$.

5. **Action of** Na_2CO_3 **:** It reacts with Na_2CO_3 solution to form basic magnesium bicarbonate.

$$2MgSO_4+Na_2CO_3+H_2O \rightarrow MgCO_3.Mg(OH)_2$$

6. Action of $NaHCO_3$: It reacts with $NaHCO_3$ solution to form $MgCO_3$.

$$MgSO_4+NaHCO_3 \rightarrow MgCO_3\downarrow+NaHSO_4$$
$$NaHCO_3+NaHSO_4 \rightarrow Na_2SO_4+CO_2\uparrow+H_2O$$
$$MgSO_4+2NaHCO_3 \rightarrow MgCO_3\downarrow+Na_2SO_4+CO_2\uparrow+H_2O$$

Uses : (i) It is used as purgative and is commonly known as Mag. sulph. (ii) In printing dyeing and tanning industries. (iii) As a laboratory reagent. (iv) As a catalyst in the manufacture of H_2SO_4 by Grillo's process.

Tests for Magnesium :

(i) **Charcoal Cavity Test :** Magnesium salts when heated strongly in a charcoal cavity leave a white residue which on heating with a drop of cobalt nitrate turns pink.

(ii) Magnesium salt solution is mixed with ammonium chloride and ammonium hydroxide and treated with a soluble hydroxide and treated with a soluble phosphate. A white precipitate of magnesium ammonium phosphate is obtained.

$$MgSO_4+NH_4OH+Na_2HPO_4 \rightarrow \underset{\text{White ppt.}}{Mg(NH_4)PO_4\downarrow}+Na_2SO_4+H_2O$$

Calcium (*Ca*)

At. No. 20. *Mass No.* 40.

Electronic configuration: $1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2$.

History : The name Calcium was derived from the latin calx (lime). In 1808 Davy prepared the metal by electrolytic method. The pure metal was obtained by Moissan in 1898 by the reduction of calcium iodide with metallic sodium.

Occurence : Calcium does not occur free in nature, but is widely distributed in the combined state. The chief calcium minerals are :

1. *Carbonate* : Lime stone, Chalk, Marble, Calcite, Ice land spar $-CaCO_3$.
2. *Sulphate* : Gypsum ($CaSO_4.2H_2O$), Anhydrite ($CaSO_4$).
3. *Fluoride* : Fluorspar (CaF_2), Fluorapatite [$3Ca_3(PO_4)_2CaF_2$]
4. *Bone* : $Ca_3(PO_4)_2$.
5. *Silicate* : Lime Felspar $Ca(AlSiO_4)_2$.

Calcium is also present in natural water, bones, egg-shells, soil, plants etc. and constitutes about 3-5 per cent of the earth crust.

Extraction : It is extracted by electrolytic method :

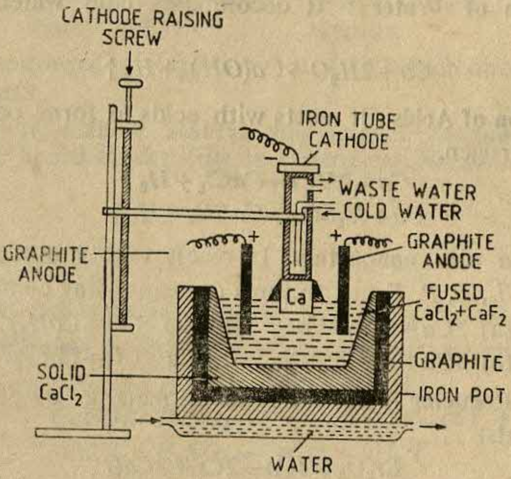
Principle : Calcium is extracted by the electrolysis of fused mixture of calcium chloride with about 16 per cent of calcium fluoride in a graphite crucible which serves as an anode. The cathode is movable iron rod which touches the surface of the fused electrolyte. A current of cold water in passed round ihe Cathode to cool the system.

$$\underset{\text{Fused}}{CaCl_2, CaF_2\ (\text{Flux})} \xrightarrow{\text{Electrolysis}} Ca^{++} + 2Cl^-$$

Cathodic Meduction $Ca^{++} + 2e \rightarrow Ca$

Anodic Oxidation $2Cl^- \rightarrow Cl_2 + 2e$

A self-explanatory diagram of the electrolytic cell is given below :



Description of the Process : (i) First of all anhydrous mixture of 84% $CaCl_2$ and 16% CaF_2 is prepared.

(ii) Electrolysis of the fused mixture using a current of 0·4 ampere square cm. of anode area at a voltage of about 10 volt are applied. As a result of electrolysis the reactions occur and Ca is deposited at the lower end of the iron cathode.

(iii) As the calcium accumulates, the cathode is screwed up in such a way that only the extreme tip of the deposited calcium is in contact with the fused electrolyte. This prevents the fusion of the metal in the bath and enables the isolation of the metal in the solid state. As electrolysis proceeds a continuous rod of calcium builds up around the cathode and itself acts as cathode. The whole plant is cooled by passing cold water.

Properties :

Physical : (i) It is silvery white, lustrous metal. (ii) It is malleable and as hard as tin. (ii) It is a light metal having sp. gr. 1·55. (iv) It melts at 810°C and boils at 1439°C.

Chemical :

(i) **Action of Air** : It is slowly tarnished in moist air. On heating it burns in air forming a mixture of oxide and a little nitride, Ca_3N_2.

$$2Ca+O_2 \rightarrow 2CaO$$
$$3Ca+N_2 \rightarrow Ca_3N_2$$

(ii) Action of Water : It decomposes cold water liberating hydrogen.

$$Ca+2H_2O \rightarrow Ca(OH)_2+H_2\uparrow$$

(iii) Action of Acids : It reacts with acids to form corresponding salts and hydrogen.

$$Ca+2HCl \rightarrow CaCl_2+H_2\uparrow$$
$$Ca+H_2SO_4 \rightarrow CaSO_4+H_2\uparrow$$

(iv) **Action with non-metals** : It reacts with non-metals such as O_2, H_2, N_2, Cl_2, S, P, F_2 etc. to form corresponding compounds.

(a) $2Ca+O_2 \rightarrow 2CaO$, (b) $Ca+H_2 \rightarrow CaH_2$,
(c) $3Ca+N_2 \rightarrow Ca_3N_2$, (d) $Ca+Cl_2 \rightarrow CaCl_2$.

(v) **As a Reducing Agent** : It reduces metallic oxides and chlorides to metals.

$$Cr_2O_3+3Ca \rightarrow 2Cr+3CaO$$
$$ZnCl_2+Ca \rightarrow Zn+CaCl_2$$

Uses : It is used :

(a) as a drying agent in the preparation of absolute alcohol.
(b) for the removal of sulphur from petroleum.

Compounds of Calcium

Hydrolith, CaH_2 :

Preparation : It is prepared by passing hydrogen over heated calcium.

$$Ca+H_2 \rightarrow CaH_2$$

Properties : It is colourless crystalline solid which reacts with water to evolve hydrogen gas.

$$CaH_2+2H_2O \rightarrow Ca(OH)_2+2H_2\uparrow$$

Uses : It is used in the preparation of pure hydrogen.

Plaster of Paris, $CaSO_4.\frac{1}{2}H_2O$ or $2CaSO_4\ H_2O$ or $(CaSO_4)_2.H_2O$:

Preparation : It is prepared by heating gypsum to 120°C.

$$\underset{\text{Gypsum}}{2[CaSO_4.2H_2O]} \xrightarrow{120°C} 2(CaSO_4).H_2O+2H_2O$$

Properties : (i) It is a white solid which forms a paste with water. This sets to a solid mass with expansion and is converted into gypsum. This is known as *setting of Plaster of Paris.*

$$\underset{\text{Plaster of Paris}}{2(CaSO_4)\ H_2O}+2H_2O \rightarrow \underset{\text{Gypsum}}{2CaSO_4.2H_2O}$$

(ii) It is converted to dead burnt at 200°C which does not possess setting property.

Uses : (i) In making statues and surgical bandages. (ii) In making black board chalks. (iii) In casting moulds. (iv) In plastering of walls.

Gypsum, $CaSO_4.2H_2O$:

Preparation : It is prepared in the laboratory by the action of dilute sulphuric acid on calcium oxide, carbonate or chloride.

$$CaO+H_2SO_4 \rightarrow CaSO_4+H_2O$$
$$CaCO_3+H_2SO_4 \rightarrow CaSO_4+H_2O+CO_2\uparrow$$
$$CaCl_2+H_2SO_4 \rightarrow CaSO_4+2HCl$$

1. **Properties :** It is white a crystalline, solid, slightly soluble in water. With rise of temperature to 40°C, the solubility increases and on further heating it falls.

2. It dissolves in ammonium sulphate solution forming the double salt, $CaSO_4.(NH_4)_2SO_4.2H_2O$.

3. **Action of Heat :** On heating to 120°C it loses 3/4th of its water of crystallization forming the semihydrate $CaSO_4.\frac{1}{2}H_2O$ or $2CaSO_4\ H_2O$ known as *Plaster of Paris.*

$$2CaSO_4.2H_2O \xrightarrow{120°C} (CaSO_4)_2H_2O+3H_2O$$

On further heating to 200°C, it forms anhydrous calcium sulphate which does not set when mixed with water. This is said to be *dead burnt gypsum.*

4. When calcium sulphate is heated with carbon it is reduced to calcium sulphide.

$$CaSO_4 + 4C \rightarrow CaS + 4CO\uparrow$$

Uses : 1. It is used in the manufacture of ammonium sulphate, which is used as an artificial fertiliser.

2. In the manufacture of cement, in making writing chalks.

3. Gypsum is also used in filling glazed paper and pottery.

4. It is used in pottery, dentistry, in moulding toys and statues.

Calcium oxide or Quick lime, CaO :

Manufacture : It is prepared by heating limestone in specially designed kilns at 900°C – 1000°C.

$$CaCO_3 \xrightarrow{900°C-1000°C} CaO + CO_2\uparrow$$

Properties : (i) It is a white solid.

(ii) When it is heated to high temperature then white light is produced. This is known as lime-light.

(iii) Action of Water : It reacts with water to give $Ca(OH)_2$. The reaction is exothermic.

$$\underset{\text{Quick lime}}{CaO} + H_2O \rightarrow \underset{\text{Slaked lime}}{Ca(OH)_2} + Q$$

(iv) Action of CO_2 : CO_2 is absorbed by CaO giving $CaCO_3$.

$$CaO + CO_2 \rightarrow CaCO_3$$

(v) Action of Chlorine : It reacts with chlorine at 40°C to give bleaching powder.

$$CaO + Cl_2 \rightarrow Ca(OCl)Cl$$

At higher temperature oxygen is obtained.

$$CaO + Cl_2 \rightarrow CaCl_2 + \tfrac{1}{2}O_2$$

(vi) Action of Acids : It reacts with acids to give salts and water.

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O$$

$$CaO + H_2SO_4 \rightarrow CaSO_4 + H_2O$$

Uses : It is used (a) in the lining of furnace, (b) in the preparation of slaked lime, (c) as a laboratory reagent, (d) as a desiccating agent for NH_3.

Super Phosphate of Lime :

Preparation : It is prepared by the action of dil. H_2SO_4 on calcium phosphate, $Ca_3(PO_4)_2$. The product consists of a dry mixture of primary calcium phosphate and gypsum and is technically known as **superphosphate of lime.**

$$Ca_3(PO_4)_2+2H_2SO_4+H_2O \rightarrow Ca(H_2PO_4)_2H_2O+2CaSO_4$$

$$CaSO_4+2H_2O \rightarrow CaSO_4.2H_2O\ [\times 2]$$

$$Ca_3(PO_4)_2+2H_2SO_4+5H_2O \rightarrow Ca(H_2PO_4)_2H_2O+2CaSO_4.2H_2O$$

The well powdered phosphate rock is placed in the mixers and calculated quantity of concentrated H_2SO_4 is also added. The whole mass is well stirred and then pumped into the dens. It is left into the dens for a day and half when a solid product separates out. It is crushed to a fine powder and is known as superphosphate of lime.

It is soluble in water and is used as a fertilizer.

Calcium cyanamide, $CaCN_2$ **(Nitrolim,** $CaCN_2+C$**) :**

Preparation : It is prepared by heating calcium carbide to about 1000°C and passing a current of dry nitrogen over it. A mixture of calcium cyanamide along with carbon is formed.

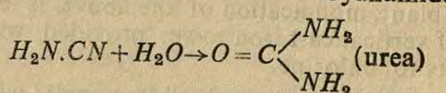
$$CaC_2+N_2 \rightarrow CaCN_2+C$$

Properties : When treated with steam, it is converted into calcium carbonate and NH_3 gas is given of

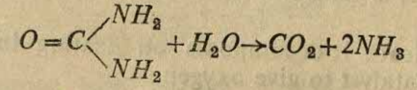
$$CaCN_2+3H_2O \rightarrow CaCO_3+2NH_3$$

When applied to the soil, a similar reaction takes place but in stages forming cyanamide and urea as intermediate products.

$$CaCN_2+H_2O+CO_2 \rightarrow CaCO_3+\underset{\text{Cyanamide}}{H_2N.CN}$$



$$H_2N.CN+H_2O \rightarrow O=C\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix}\ \text{(urea)}$$



$$O=C\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix}+H_2O \rightarrow CO_2+2NH_3$$

Uses : (i) As a fertilizer under the name of ***Nitrolim*** which is actually mixture of calcium cyanamide and carbon.

(ii) In the preparation of NH_3.

Bleaching Powder, $Ca(OCl)Cl$ **or** $CaCl_2.Ca(OCl)_2$ **:**

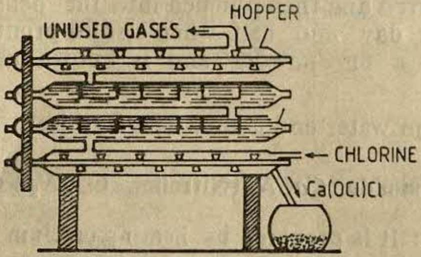
Principle of Manufacture : It is manufactured on large scale by the action of chlorine on dry slaked lime at 40°C. There are two views regarding the chemistry of the reaction.

First view (Odling's)

$$Ca(OH)_2+Cl_2 \rightarrow \underset{\text{Bleaching powder.}}{Ca(OCl)Cl}+H_2O$$

Second view (Clifford's)

$$\begin{array}{l} 2Ca(OH)_2+2Cl_2 \rightarrow \underset{\text{Calcium hypochlorite}}{Ca(OCl)_2} + CaCl_2+2H_2O \\ CaCl_2+Ca(OH)_2+H_2O \rightarrow CaCl_2.Ca(OH)_2\,H_2O \\ \hline 3Ca(OH)_2+2Cl_2 \rightarrow \underbrace{Ca(OCl)_2+CaCl_2\,Ca(OH)_2.H_2O}_{\text{Bleaching Powder}}+H_2O \end{array}$$



Manufacture of Bleaching Powder

The plant commonly used is due to *Hesenclever* and consists of a number of horizontal cylinders containing a rotating shaft, fitted with blades. The lime introduced through the hopper is made to move from one end of the cylinder to the other by the blades. Chlorine gas is introduced from the bottom and passes upwards. The plant thus works on the *counter current principle* and ensures maximum absorption of lime. The bleaching powder formed is collected in the drums as shown in the diagram.

Another plant, modification of the above, is due to *Bachmann*. It consists of vertical cast iron tower provided with hopper at the top and inlets for chlorine.

(i) Properties : It is yellowish white powder with a strong smell of chlorine.

(ii) Action of Heat : It decomposes on heating in presence of cobalt chloride as catalyst to give oxygen.

$$2Ca(OCl)Cl \rightarrow 2CaCl_2+O_2$$

(iii) Reaction with Acids : It liberates whole chlorine with dil. HCl or H_2SO_4. It is known as available chlorine.

(a)

$$\begin{array}{c} 2Ca(OCl)Cl \rightarrow CaO+Cl_2 \\ CaO+H_2SO_4 \rightarrow CaSO_4+H_2O \\ \hline Ca(OCl)Cl+H_2SO_4 \rightarrow CaSO_4+H_2O+Cl_2 \end{array}$$

(b)

$$\begin{array}{c} Ca(OCl)Cl \rightarrow CaO+Cl_2 \\ CaO+2HCl \rightarrow CaCl_2+H_2O \\ \hline Ca(OCl)Cl+2HCl \rightarrow CaCl_2+Cl_2+H_2O \end{array}$$

(c)

$$\begin{array}{c} Ca(OCl)Cl \rightarrow CaO+Cl_2 \\ CaO+CO_2 \rightarrow CaCO_3 \\ \hline Ca(OCl)Cl+CO_2 \rightarrow CaCO_3+Cl_2 \end{array}$$

(iv) Reaction with Alcohol or Acetone : It forms chloroform with ethyl alcohol or acetone. It acts both as chlorinating and hydrolysing agent.

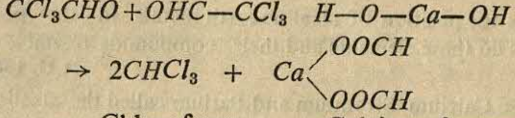
(a)

$$Ca(OCl)Cl + H_2O \rightarrow Ca(OH)_2 + Cl_2$$

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + Cl_2 \rightarrow \underset{\text{Actaldehyde}}{CH_3CHO} + 2HCl$$

$$CH_3CHO + 3Cl_2 \rightarrow CCl_3.CHO + 3HCl$$

Chloral
or, trichloro acetaldehyde

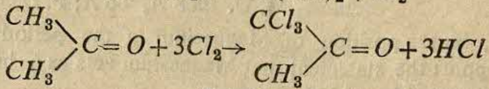


$$CCl_3CHO + OHC{-}CCl_3 \quad H{-}O{-}Ca{-}OH \rightarrow 2CHCl_3 + Ca\begin{cases} OOCH \\ OOCH \end{cases}$$

Chloroform Calcium formate

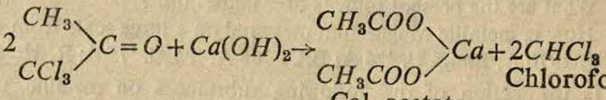
(b)

$$Ca(OCl)Cl + H_2O \rightarrow Ca(OH)_2 + Cl_2$$



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\Big\rangle C{=}O + 3Cl_2 \rightarrow \begin{matrix} CCl_3 \\ CH_3 \end{matrix}\Big\rangle C{=}O + 3HCl$$

Trichloro acetone

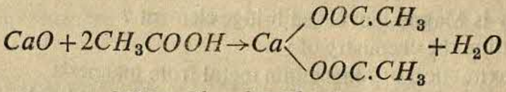


$$2\begin{matrix} CH_3 \\ CCl_3 \end{matrix}\Big\rangle C{=}O + Ca(OH)_2 \rightarrow \begin{matrix} CH_3COO \\ CH_3COO \end{matrix}\Big\rangle Ca + 2CHCl_3$$

Cal. acetate Chloroform

(v) Reaction with Potassium iodide and Acetic acid : It oxidises potassium iodide to iodine.

$$Ca(OCl)Cl \rightarrow CaO + Cl_2$$



$$CaO + 2CH_3COOH \rightarrow Ca\begin{cases} OOC.CH_3 \\ OOC.CH_3 \end{cases} + H_2O$$

$$2KI + Cl_2 \rightarrow 2KCl + I_2$$

$$\overline{Ca(OCl)Cl + 2CH_3COOH + 2KI \rightarrow Ca(CH_3COO)_2 + H_2O + I_2 + 2KCl.}$$

(vi) Reaction with Sodium Arsenite : It oxidises arsenite to arsenate.

$$Ca(OCl)Cl \rightarrow CaO + Cl_2$$

$$Na_3AsO_3 + H_2O + Cl_2 \rightarrow Na_3AsO_4 + 2HCl$$

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O$$

$$\overline{Na_3AsO_3 + H_2O + Ca(OCl)Cl \rightarrow CaCl_2 + Na_3AsO_4}$$

(vii) Reaction with Ammonia : It oxidises ammonia to nitrogen.

$$Ca(OCl)Cl \rightarrow CaCl_2 + \text{'}O\text{'} \; [\times 3]$$

$$2NH_3 + 3\text{'}O\text{'} \rightarrow N_2 + 3H_2O$$

$$\overline{3Ca(OCl)Cl + 2NH_3 \rightarrow N_2 + 3H_2O + 3CaCl_2}$$

Uses : 1. Bleaching agent for wood.

2. Disinfectant and germicide for killing disease germs i.e. cholera, in drinking water.

3. In the manufacture of chloroform.

4. Making wool unshrinkable.

QUESTIONS

Long and Short Type Questions :

1. Discuss the position of alkaline earth metals in the periodic table. In what respects do these elements and their compounds resemble one another ?

(R.U. 1966 A; P.U. '70 A)

2. Why are Calcium, Strontium and Barium called the alkaline earth metals ? Compare of its compounds with Strontium, Barium and their corresponding compounds. Record your answer in a tabular form.

(M. U. 1965 A, '66 A; P. U. '70 A; B. U. '71 A)

3. Discuss, on the position of Magnesium in the periodic table. Examine the facts to support the statement that Magnesium acts as a bridge element between the subgroups IIA and IIB.

4. (a) What are the present sources of Magnesium ? (M. U. 1973)

(b) How is metallic Magnesium prepared on a large scale from carnallite ?

(P. U. 1970 A; Bhag. U. '76 A; B.U. '66 A; M.U. '75 A; R. U. '68 A, '74 S)

What is the action of the following substances on metallic magnesium ? (a) water, (b) air, (c) chlorine, and (d) nitric acid. (M. U. 1975 A)

5. Discuss the position of Magnesium in the periodic table. Mention its important ores. Describe one method for its extraction. What are the uses of Magnesium ?

(M. U. 1964 A; P. U. '63 A)

6. (a) Why is Magnesium called bridge element ?

(b) Outline the chemistry of :

(i) extraction of Magnesium metal from magnesia

and (ii) preparation of anhydrous magnesium chloride from magnesium metal.

(P.U. 1976 A)

7. How is Magnesium obtained from sea water ?

What properties show that Magnesium is a metal ?

Under what conditions and with what results does it react with (a) water, (b) nitrogen, (c) hydrogen chloride, (d) copper sulphate solution ?

(R. U. 1976; B. U. '64 A; Bhag. U. '68 A)

8. How does calcium occur in nature ? Outline the steps by which metallic calcium is obtained.

Describe the action of heat on the compounds : (i) $CaSO_4.2H_2O$, (ii) $CaCl_2.6H_2O$, (iii) $CaCO_3$. State in each case how the solid product obtained behaves with water.

9. What are the common sources of quick lime in this country ? How is it manufactured ? Describe its properties and uses.

(M. U. 1963 A; B. U. '66 A; P. U. '71 S)

10. Describe the preparation, properties and uses of :

(i) Bleaching Powder. **(P. U. 1966 A; B. U. '68 A; R. U. '68 A)**

(ii) Gypsum. **(BIEC. 1984; M.U. '81)**

(iii) Plaster of Paris. **(M.U. 1981)**

(iv) Quick lime.

(v) Nitrolim.

(vi) Epsom Salt. **(M.U. 1981)**

11. Match A with B.

Formula A	*Trade Name B*
1. MgO	(a) Epsom Salt
2 $MgCO_3$	(b) Quick lime
3. $MgSO_4.7H_2O$	(c) Magnesia
4. CaO	(d) Milk of magnesia
5. $Mg(OH)_2$	(e) Gypsum
6. $CaSO_4.2H_2O$	(f) Plaster of Paris
7. $CaSO_4\ 1/2H_2O$	(g) Slaked lime
8. $Ca(OH)_2$	(h) Magnesite.

12. Write down the chemical formula of the following mentioning one use of each.

(1) Plaster of Paris, (2) Gypsum, (3) Quick lime, (4) Epsom Salt, (5) Anhydrous Magnesium chloride, (6) Slaked lime, (7) Calcium carbide, (8) Lithopone, (9) Soda lime, (10) Superphosphate of lime.

13. Fill up the blank:

(i) The formula of Plaster of Paris is......... (ii) Quick lime is used for......... of NH_3. (iii) Epsom Salt is used as......... (iv) Calcium carbide gives.........with water. (v) Superphosphate of lime is used in......... . (vi) Ca is a.........block element. (vii) Calcium belongs to.........period and......... A such group of the periodic table.

14. What happens when:

(i) hydrated Magnesium chloride is heated strongly ?

(ii) Na_2CO_3 solution is added to Magnesium chloride solution ?

(iii) $NaHCO_3$ solution is added to $MgSO_4$ solution ?

(iv) Gypsum is heated to 120°C ?

(v) Bleaching powder is added to Ethyl alcohol ?

(vi) Bleaching powder is added to mixture of KI and CH_3COOH.

(vii) Excess of CO_2 is passed into lime water.

Objective Question

Select and Write the Correct from the following :

15. Which of the following is a member of 4th period and IIA of the periodic table ?

(1) Mg, (2) Ca, (3) Al, (4) all the above, (5) more than one.

16. Which of the following is obtained when Gypsum is heated to 200°C ?

(1) $CaSO_4H_2O$, (2) $CaSO_4.1/2H_2O$, (3) $CaSO_4$, (4) $CaO+SO_3$.

17. Which of the following compounds of Magnesium is used as purgative ?

(1) Epsom Salt, (2) Magnesia, (3) Dolomite, (4) Magnesium Oxide.

18. Which one of the following metal oxide is the most basic ?

(1) MgO, (2) CaO, (3) BaO, (4) SrO.

19. Which one of the following is the formula of bleaching powder ?

(1) $Ca(OCl)_2$, (2) $CaCl_2$, (3) $CaCl_2\ Ca(OCl)_2$, (4) $Ca(OH)_2$. **(BIEC. 1983)**

20. Important ore of Magnesium is :

(1) Dolomite, (2) Apatite, (3) Gypsum, (4) Fluor apatite.

21. A compound when mixed with water gives hissing sound and becomes very hot. It is

(1) Slaked lime, (2) Quick lime, (3) Iceland spar, (4) Dolomite.

22. Which of the following is a bridge metal ?

(1) Ca, (2) Mg, (3) Ba, (4) Sr, (5) Cu.

23. A substance which gives a brick red flame test and breaks down when heated to give both oxygen and a brown gas is :

(1) $Ca(HCO_3)_2$, (2) $Mg(NO_3)_2$, (3) $Ca(NO_3)_2$, (4) $NaNO_3$.

24. Pure anhydrous $MgCl_2$ can be prepared from the hydrated salt by heating the hydrate :

(1) with magnesium powder, (2) with coke, (3) in a current of HCl gas, (4) until it fuses.

25. Which of the following is used in tooth powder and face powder ?

(1) $MgCO_3$, (2) $BaCO_3$, (3) $SrCO_3$, (4) $CaCO_3$.

26. Which of the following gives hydrogen with water ?

(1) Slaked lime, (2) Hydrolith, (3) Lithopone, (4) Calcium carbide.

27. Which ore of Magnesium contains Magnesium carbonate ?

(1) Carnallite, (2) Epsomite, (3) Dolomite, (4) Magnesia.

28. Plaster of Paris is :

(1) $CaSO_4.2H_2O$, (2) $CaSO_4.H_2O$, (3) $CaSO_41/2H_2O$, (4) $2CaSO_4.H_2O$, (5) More than one.

29. Plaster of Paris :
(1) expands while setting,
(2) contracts while setting,
(3) no change takes place while setting,
(4) becomes half of the initial volume while setting.

30. The Magnesium compound dissolved in sea water in great quantity is :
(1) Magnesium oxide, (2) Magnesium bromide, (3) Magnesium nitrate,
(4) Magnesium sulphide.

31. Quick lime is produced commercially by heating
(1) $CaCl_2$, (2) $CaCO_3$, (3) $Ca(OH)_2$, (4) $Ca_3(PO_4)_2$.

32. A water suspension of calcium hydroxide is known as :
(1) Quick lime, (2) Lime water. (3) Milk of lime, (4) Cement.

* * *

CHAPTER 16

STUDY OF GROUP II-B OF ELEMENTS

(Zn, Cd, Hg)

16.1. Periodic Discussion :

The group II-B of the periodic table includes three transitional elements *Zn*, *Cd* and *Hg*. The coinage metals *Cu*, *Ag* and *Au* are their neighbours on the left and *Ga*, *In* and *Tl* on the right. These elements show marked resemblance and a regular gradation in their properties with the rise of atomic weight. The properties given below which justifies their inclusion in the same group of the periodic table.

Resemblances :

(i) **Occurenee** : They do not occur in the free state in nature. The important ores are those of sulphides.

(ii) **Extraction** : They are obtained by similar methods from their sulphides i.e. by the dry process of roasting and smelting.

(iii) **Electronic Arrangment :**

$_{30}Zn$......2, 8, 18, 2
$_{48}Cd$......2, 8, 18, 18, 2
$_{80}Hg$......2, 8, 18, 32, 18, 2

They contain 2 valency electrons. The penultimate orbit contains 18 electrons. They do not exhibit variable valency. Due to the small atomic volume of these metals, the positive nucleus exerts a strong influence at the periphery of the atom. Hence the electrons from the penultimate orbit are never used for valency purposes.

(iv) **Action of Air** : They are oxidised very slowly in air but on heating form oxides.

$$2Zn + O_2 \rightarrow 2ZnO$$

(v) **Action of Water** : They are very slowly affected by water.

(vi) **Action of Acids** : *Zn* and *Cd* readily dissolve in acid, evolving hydrogen or oxides of N_2 and NH_3 with HNO_3. *Hg* is not attacted by dilute acids.

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$
$$Zn + 4HNO_3 \rightarrow Zn(NO_3)_2 + 2NO_2 \uparrow + 2H_2O$$

(vii) Complex Formation : These form complex salts of the type

$$[Zn(NH_3)_4]SO_4 \quad [Cd(NH_3)_4]SO_4 \quad HgNH_2Cl$$
$$K_2[Zn(CN)_4] \quad K_2[Cd(CN)_4] \quad K_2[HgI_4]$$

(viii) Action of $NaOH$: They form precipitates of Zn and Cd hydroxides from their salt solutions, former being soluble in excess, the latter insoluble. Hg salts give mercury oxide.

$$ZnSO_4+2NaOH \rightarrow Zn(OH)_2+Na_2SO_4$$
$$ZnSO_4+4NaOH \rightarrow Na_2ZnO_2+Na_2SO_4+2H_2O$$
$$HgCl_2+2NaOH \rightarrow Hg(OH)_2+2NaCl$$
$$Hg(OH)_2 \rightarrow HgO+H_2O$$

(ix) Action of Organic Substances : Due to covalent nature these elements give Alkyl compounds. i.e. $[M(CH_3)_2]$, M is Zn, Cd, Hg.

Generalities of Their Salts :

(i) Chlorides : They have low melting point. They are volatile. They are freely soluble in organic solvents. $HgCl_2$ is very slightly ionised in solution.

(ii) Nitrates, Sulphates, Carbonates, Hydroxides etc. : They decompose on heating.

(iii) Sulphides : They are insoluble in acidic medium or neutral medium. Sulphides are coloured.

(iv) Sulphates : They are readily soluble.

(v) Oxides : They are insoluble and coloured.

(vi) Hydroxides : They are less basic. The thermal stability gradually decreases from Zn towards Hg as shown below :

$$ZnO > CdO > HgO$$

Gradation :

(i) Density Increases and m.p. and b.p. decrease with the rise of atomic weight. Some of the physical properties are given below :

Metal	Density	M.P. 0°C	B.P. 0°C	Specific heat
Zn	7·74	419·4	920	0·093
Cd	8·64	321·0	767	0·053
Hg	13·46	38·8	356·7	0·033

(ii) The malleability and ductility decrease.

(iii) Electropositive nature and reactivity decreases with the rise of atomic weight.

(iv) The basicity increases with the rise of atomic weight.

(v) The decomposition of the salts like nitrates, carbonates, sulphates, and hydroxides becomes easier with the rise of atomic weight. *Hg* salts even give the metal in some cases.

(vi) The solubility of the sulphide decreases from *Zn* to *Hg*. *ZnS* is soluble in dil. *HCl*, *CdS* in conc. *HCl* and *HgS* is soluble only in aqua regia.

(vii) All the elements form stable complexes readily. The important ligands are ammonia, amines, cyanide ions etc.

Example : $[Zn(NH_3)_4SO_4]$, $K_2[Cd(CN)_4]$, $K_2[HgI_4]$

16.2. Zinc

Symbol : *Zn* *At. No.* : 30 *At. wt.* : 65·37.

Electronic configuration : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$.

Occurence : Zinc occurs mainly in combined state. Some of the important ores are given below :

Zinc Spinal....$ZnAl_2O_4$
Willemite.... Zn_2SiO_4
Franklinite....$Zn(FeO_2)_2$
Zinc blende....ZnS
Calamine......$ZnCO_3$
Zincite.... ZnO.

The most important ore from which the largest amount of the world's production of zinc is derived is zinc blende. In India it is found in Zawar (Raj.), Kashmir. The next importance ore is calamine.

Extraction :

The metal is extracted by the following methods—

1. **Reduction Process** : It involves the following methods :

(i) **Concentration** : When the ore is zinc blende it is concentrated by 'froth floatation process'. The powdered ore is suspended in water and after adding little pine oil, it is stirred by means of a blast of air. The particles of the sulphide ore being preferentially wetted by the oil, come to the surface along with the froth and are removed.

The gangue particles remain at the bottom and are rejected.

(ii) **Roasting** : The concentrated ore is then heated to about 900°C in excess of air whereby it is oxidised into zinc oxide.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

If calamine is used it is calcined to get the oxide.

$$ZnCO_3 \rightarrow ZnO + CO_2$$

(iii) Reduction : Zinc oxide obtained as above is reduced to metal by heating it with coal in fire clay retort.

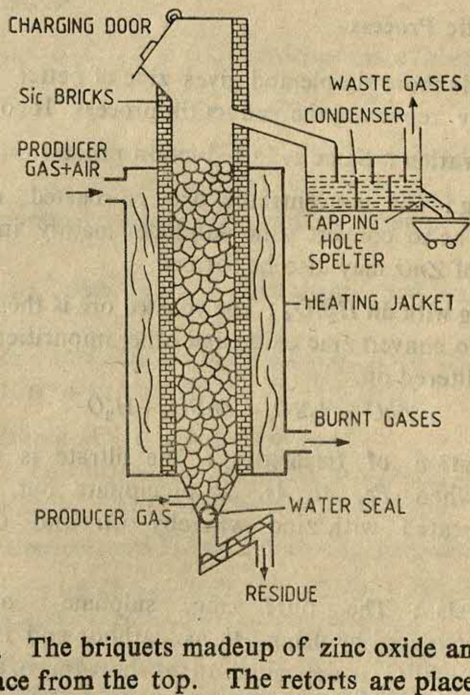
$$ZnO + C \rightarrow Zn + CO$$

The shape of the retorts differ with the process employed.

(a) Belgian Process : This is an old process. Hence the cylindrical retorts are arranged in several rows in the furnace. The mouth of each retort is provided with earthenware condenser cooled by air.

When the retorts are heated by burning producer gas, the metal zinc formed volatilises off and is collected in receivers partly as fused metal (called *spelter*) and partly as powder (called *zinc dust*).

(b) Vertical Retort Process : This is the modern process and being continuous and economical, it is rapidly replacing the old Belgian process. Here vertical retorts which are about 25 feet high are used. The briquets madeup of zinc oxide and coke are fed into the furnace from the top. The retorts are placed in a furnace heated by burning producer gas to about 1400°C. The vapour of zinc and carbon monoxide gas produced in the process are



carried in the condensers by the current of producer gas admitted at the bottom of the retort. Zinc condenses and the liquid is tapped off.

(iv) Purification of Zinc : Zinc so obtained contains Pb, Fe, Cd, As, Sb as chief impurities. It is purified by two methods :

(a) By Fractional Distillation : The boiling point of Pb (1755°C) and Fe (2800°C) are higher than that of zinc (907°C) while that of Cd (767°C) is lower. Thus when the distillation is carried out around 1000°C only zinc and cadmium distil over leaving behind Pb and Fe. Impure Zn is then distilled at about 800°C when Cd distils off leaving behind Zn which is about 99·9% pure.

(b) By electrolysis : The impure metal is made the anode and the cathode consists of sheet of pure aluminium. A solution of $ZnSO_4$ containing a little dilute. H_2SO_4 acts as an electrolyte. Zinc dissolves and deposits on cathode from which it is scrapped off.

2. Electrolytic Process :

The process is more simple and gives zinc of better quality and is thus gradually replacing the reduction process. It consists of :

(i) Concentration : Same as in reduction process.

(ii) Roasting : The concentrated ore is roasted at moderate temperature so as to convert zinc sulphide mainly into zinc sulphate. A part of ZnO may also be formed.

(iii) Leaching with dil H_2SO_4 : The roasted ore is then dissolved in dilute. H_2SO_4 to convert zinc oxide and other impurities into soluble sulphates and filtered off.

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$$

(iv) Precipitation of Impurities : The filtrate is treated with milk of lime when Fe, Al, As, Sb precipitate out. It is again filtered and treated with zinc whereby Cu and Cd also get precipitated.

(v) Electrolysis : The pure zinc sulphate solution thus obtained is electrolysed by using Al as cathode and Pb as anode. Pure zinc (m. p. 420°C) is deposited on Al sheet (m. p. 600°C) from where it is scraped off. It is then melted and cast into sticks (99·97%) metal.

Properties of Zinc :

Physical : (i) In pure state it is bluish white metal but changes to a grey colour when exposed to moist air.

(ii) Its specific gravity is 7·14, melting point is 419°C and boiling point is 907°C.

(iii) It forms alloys with large number of metals.

(iv) It is good conductor of heat and electricity.

Chemical :

(i) Action of Air : Zinc is not attacked by dry air at ordinary conditions. When heated in air to over 100°C, zinc burns with a bluish white flame forming zinc oxide.

$$2Zn + O_2 \rightarrow 2ZnO.$$

(ii) Action of Water : Pure zinc is not attacked by water. The commercial zinc decomposes boiling water, evolving hydrogen.

$$Zn + H_2O \rightarrow ZnO + H_2 \uparrow$$

3. **Action of Acids :**

(a) With dil. H_2SO_4 and HCl, hydrogen is evolved.

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2 \uparrow$$
$$Zn + 2HCl \rightarrow ZnCl_2 + H_2 \uparrow$$

(b) With hot concentrated H_2SO_4, SO_2 is evolved.

$$Zn + 2H_2SO_4 \rightarrow ZnSO_4 + 2H_2O + SO_2 \uparrow$$

(c) The reaction with nitric acid is different under different conditions.

(i) With very Dilute HNO_3 : Zinc nitrate and ammonium nitrate are formed.

$$4Zn + 10HNO_3 \rightarrow 4Zn(NO_3) + NH_4NO_3 + 3H_2O$$
$$(4Zn + 10H^+ + NO_3^- \rightarrow 4Zn^{+2} + NH_4^+ + 3H_2O)$$

(ii) With Dilute HNO_2 : N_2O is evolved.

$$4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

or $(4Zn + 2NO_3^- + 10H^+ \rightarrow 4Zn^{+2} + N_2O + 5H_2O)$

(iii) With Concentrated HNO_3 : Nitrogen peroxide is formed.

$$Zn + 4HNO_3 \rightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$$
$$(Zn + NO_3^- + 4H^+ \rightarrow Zn^{+2} + 2NO_2 + 2H_2O)$$

(iv) With Moderate HNO_3 : Nitric oxide is formed.

$$3Zn + 8HNO_3 \rightarrow 3Zn(NO_3)_2 + 2NO + 4H_2O$$
$$(3Zn + 8H^+ + 2NO_3^- \rightarrow 3Zn^{+2} + 2NO + 4H_2O)$$

4. **Action of Alkalies :** Zinc dissolved in alkalies evolving hydrogen and forming soluble zincates. In zincates the zinc atom is contained in a comples hydroxoanion e.g.

$$Zn+2OH^-+2H_2O \rightarrow Zn(OH)_4^{2-}+H_2\uparrow$$

or $$Zn+2NaOH \rightarrow Na_2ZnO_2+H_2\uparrow$$

5. **Action of Chlorine and Sulphur :** On heating it forms chlorides and sulphides respectively.

(a) $$Zn+Cl_2 \rightarrow ZnCl_2$$

(b) $$Zn+S \rightarrow ZnS.$$

6. **Action of Solutions of salts :** Zinc replaces less electropositive metals from their salt solutions :

(a) $$CuSO_4+Zn \rightarrow ZnSO_4+Cu$$

or (b) $$Cu^{+2}+Zn \rightarrow Zn^{+2}+Cu$$

7. **Action of Alkylhalides :** At ordinary temperatures, zinc forms an addition compound with an alkyl halide.

$$Zn+C_2H_5I \rightarrow \underset{\text{Ethyl zinc iodide.}}{C_2H_5ZnI}$$

The compound break up on heating

$$2C_2H_5ZnI \rightarrow \underset{\text{Zinc diethyl}}{Zn(C_2H_5)_2} + ZnI_2$$

or in general

$$Zn+R-X \rightarrow RZnX$$

$$2RZnX \rightarrow R_2Zn + ZnX_2$$

Zinc alkyls

Zinc alkyls are vile-smelling inflammable liquids. They react with water forming an alkane.

$$R_2Zn+2H_2O \rightarrow Zn(OH)_2+2R-H$$

e.g. $$Zn(C_2H_5)_2+2H_2O \rightarrow Zn(OH)_2+\underset{\text{(Ethane)}}{2C_2H_6}$$

Zinc alkyls were the first **Organo-Metalic** compounds, prepared by Frankland in 1849.

Uses of Zinc :

(i) *Zn* dust as an important reducing' agent in the laboratory and in the manufacture of dyes, drugs, and artificial perfumes.

(ii) Zinc sheets for roofs, gutters etc.

(iii) Zinc metal is used in wet and dry Leclanche batteries.

(iv) Smaller iron articles may be coated by heating with zinc dust. This process is known as **sherardizing.**

(v) In preparing several useful alloys like Brass, German silver, zinc bronze etc.

16.3. Compounds of Zinc :

1. Zinc Oxide, or Philosopher's wool (ZnO)

Preparation :

(i) It is obtained by heating zinc in air or by strongly heating zinc carbonate, nitrate or hydroxide.

(a) $2Zn + O_2 \rightarrow 2ZnO$

(b) $Zn(OH)_2 \rightarrow ZnO + H_2O$

(c) $ZnCO_3 \rightarrow ZnO + CO_2$

(d) $2Zn(NO_3)_2 \rightarrow ZnO + 4NO_2 + O_2$.

(ii) It is also obtained by roasting the mineral zinc blende (ZnS)

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

Properties :

(i) It is white amorphous powder, insoluble in water.

(ii) It is **amphoteric** in nature, thus dissolves both in acids and alkalies.

Reaction with Acids $\begin{cases} ZnO + 2HCl \rightarrow ZnCl_2 + H_2O \\ ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O \end{cases}$

Reaction with Alkalis $\begin{cases} ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O \\ ZnO + 2KOH \rightarrow K_2ZnO_2 + H_2O \end{cases}$

Pot. Zincate.

(iii) If heated alone it turns yellow, but becomes white on cooling.

When heated with cobalt nitrate $Co(NO_3)_2$ a green coloured substance cobalt zincate, $CoZnO_2$ known as **Rienmann's Green** is obtained.

$$2Co(NO_3)_2 \rightarrow 2CoO + 4NO_2\uparrow + O_2\uparrow$$

$CoO + ZnO \rightarrow CoO.ZnO$ or $CoZnO_2$ (Cobalt zincate)

Uses : (i) It is used as pigment in white paints under the name *Chinese white* or *zinc white*. It does not turn black on exposure to H_2S like white lead and is therefore, preferred over other paints although it has low covering power.

(ii) It is used as a "filler" in dental cavities, soft rubbers, oil clothing glazed enamels.

(iii) It is used in ointment in surgical dressings and in creams used as cosmetics.

(iv) It finds use in making white ink.

2. Zinc Hydroxide, $Zn(OH)_2$:

Preparation :

It is obtained as a white precipitate when required amount of an alkali is added to a solution of zinc salt.

$$ZnSO_4 + 2NaOH \rightarrow Zn(OH)_2 + Na_2SO_4$$
$$Zn(NO_3)_2 + 2NaOH \rightarrow Zn(OH)_2 + 2NaNO_3$$

Properties :

(i) It is white insoluble substance and decomposes on heating

$$Zn(OH)_2 \rightarrow ZnO + H_2O$$

(ii) It is amphoteric in nature and reacts with both acids and alkalies.

(a) Reaction with Acids :

(i) $$Zn(OH)_2 + 2HCl \rightarrow ZnCl_2 + 2H_2O$$
(ii) $$Zn(OH)_2 + H_2SO_4 \rightarrow ZnSO_4 + 2H_2O$$

(b) Reaction with Alkalies :

$$Zn(OH)_2 + 2NaOH \rightarrow Na_2ZnO_2 + 2H_2O$$

It must be noted that it does not form ammonium zincate with ammonia but forms complex ion $[Zn(NH_3)_4]^{+2}$

$$Zn(OH)_2 + 4NH_3 \rightarrow [Zn(NH_3)_4]^{++}(OH)_2.$$

3. Zinc Chloride, $ZnCl_2.2H_2O$:

Preparation :

(i) It is obtained by dissolving the metal, its oxide, hydroxide or carbonate with dil. HCl. when the solution is evaporated, in presence of hydrochloric acid, crystals of $ZnCl_2.2H_2O$ are obtained.

(a) $$Zn + 2HCl \rightarrow ZnCl_2 + H_2 \uparrow$$
(b) $$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$$

(ii) Anhydrous Zinc Chloride is obtained by passing dry chlorine (Cl_2) or HCl gas on heated zinc or distilling zinc with mercuric chloride.

(a) $Zn+Cl_2 \rightarrow ZnCl_2$

(b) $Zn+2HCl \rightarrow ZnCl_2+H_2\uparrow$

(c) $Zn+HgCl_2 \rightarrow ZnCl_2+Hg.$

Properties :

(i) It is a white crystalline, **deliquescent** substance.

(ii) It is highly soluble in water. Its aqueous solution is strongly acidic due to hydrolysis.

$$ZnCl_2+H_2O \rightarrow Zn(OH)Cl+HCl.$$

(iii) It is also soluble in alcohol.

(iv) Reaction with Na_2CO_3 : It reacts with sodium carbonate solution to give basic zinc carbonate.

$$\underset{\text{solution}}{2ZnCl_2}+\underset{\text{solution}}{2Na_2CO_3}+H_2O \rightarrow \underset{\text{Basic zinc carbonate}}{ZnCO_3.Zn(OH)_2}+4NaCl+CO_2.$$

(v) Reaction with $NaHCO_3$ (Sodium bicarbonate) : It reacts with $NaHCO_3$ solution to give white precipitate of normal zinc carbonate.

$$ZnCl_2+NaHCO_3 \rightarrow ZnCO_3+NaCl+HCl$$
$$NaHCO_3+HCl \rightarrow NaCl+H_2O+CO_2$$
$$\overline{ZnCl_2+2NaHCO_3 \rightarrow ZnCO_3+2NaCl+H_2O+CO_2\uparrow}$$

(vi) Reaction with MOH ($M=Na, K$) Solution : When solution of zinc chloride reacts with $NaOH$ solution then first of all white precipitate of $Zn(OH)_2$ is obtained which is soluble in excess of $NaOH$ solution forming sodium zincate.

(a) Little $NaOH$ Solution :

$$ZnCl_2+2NaOH \rightarrow Zn(OH)_2+2NaCl$$

(b) Excess $NaOH$ Solution :

$$ZnCl_2+4NaOH \rightarrow \underset{\text{Sod. Zincate.}}{Na_2ZnO_2}+2NaCl+2H_2O$$

(vii) Reaction with Ammonia : It reacts with ammonia to form addition compound as $ZnCl_2.xNH_3$.

$$ZnCl_2+xNH_3 \rightarrow ZnCl_2.xNH_3.$$

(viii) Its concentrated solution dissolves cellulose hence it cannot be filtered through a filter paper.

Uses : (i) Anhydrous $ZnCl_2$ is used as desiccating agent, (ii) As a preservative for timber, (iii) For making parchment paper and fibre board, (iv) In surgery, (v) In dissolving cotton and cellulose, (vi) In dry cells, and as a flux in soldering.

4. Zinc Carbonate ($ZnCO_3$) :

Preparation :

It is prepared by the action of $NaHCO_3$ solution to the hot solution of the salts.

$$ZnSO_4+2NaHCO_3 \rightarrow ZnCO_3+Na_2SO_4+H_2O+CO_2\uparrow$$
$$Zn(NO_3)_2+2NaHCO_3 \rightarrow ZnCO_3+2NaNO_3+H_2O+CO_2\uparrow$$

Properties :

(i) It is amorphous white solid.
(ii) It is insoluble in water.
(iii) It is soluble in acids forming soluble salts.

$$ZnCO_3+2HCl \rightarrow ZnCl_2+H_2O+CO_2\uparrow$$
$$ZnCO_3+H_2SO_4 \rightarrow ZnSO_4+H_2O+CO_2\uparrow$$

Use : It is used as medicine in skin diseases.

5. Zinc Nitrate, $Zn(NO_3)_2.6H_2O$:

Preparation :

It is formed by the dissolution of zinc, its oxide, hydroxide, carbonates in dilute nitric acid.

(a) $ZnO+2HNO_3 \rightarrow Zn(NO_3)_2+H_2O$

(b) $Zn(OH)_2+2HNO_3 \rightarrow Zn(NO_3)_2+2H_2O$

Properties :

(i) It is a colourless, deliquescent solid, soluble in water and alcohol.

(ii) **Action of Heat :** It decomposes on heating

$$2Zn(NO_3)_2 \rightarrow 2ZnO+4NO_2\uparrow+O_2\uparrow$$

(iii) **Action of Na_2CO_3 Solution :** When Na_2CO_3 solution is added to zinc nitrate solution then basic zinc carbonate is obtained.

$$2Zn(NO_3)_2+2Na_2CO_3+H_2O \rightarrow \underset{\text{Basic zinc carbonate.}}{ZnCO_3.Zn(OH)_2}+4NaNO_3+CO_2$$

(iv) **Action of $NaHCO_3$ Solution :** When $NaHCO_3$ solution is added to zinc nitrate solution then white precipitate of zinc carbonate is obtained.

$$\begin{array}{c} Zn(NO_3)_2+NaHCO_3 \rightarrow ZnCO_3+NaNO_3+HNO_3 \\ NaHCO_3+HNO_3 \rightarrow NaNO_3+H_2O+CO_2 \\ \hline Zn(NO_3)_2+2NaHCO_3 \rightarrow ZnCO_3+2NaNO_3+H_2O+CO_2 \end{array}$$

6. Zinc Sulphate or White Vitriol, $ZnSO_4.7H_2O$

Preparation :

(i) It is prepared on commercial scale by heating zinc blende in excess of air.

$$ZnS+2O_2 \rightarrow ZnSO_4$$

(ii) It is also prepared by the action of dil. H_2SO_4 on metallic zinc, its oxide, or carbonate and evaporating the solution to crystallisation.

(a) $$Zn+H_2SO_4 \rightarrow ZnSO_4+H_2\uparrow$$

(b) $$ZnO+H_2SO_4 \rightarrow ZnSO_4+H_2O$$

Properties :

(i) It is a colourless crystalline solid.

(ii) It is highly soluble in water.

(iii) It is an **efflorescent** substance.

(iv) It is **isomorphous** with Epsom salt ($MgSO_4.7H_2O$)

(v) **Action of Heat** : On heating it becomes anhydrous and then finally decompose to ZnO, O_2 and SO_2 as

$$ZnSO_4.7H_2O \rightarrow ZnSO_4.H_2O \rightarrow ZnSO_4$$

$$\downarrow 767°C$$

$$ZnO+O_2\uparrow+SO_2\uparrow$$

(vi) **Action of Na_2CO_3 Solution** : Its solution gives basic zinc carbonate with Na_2CO_3 solution.

$$2ZnSO_4+2Na_2CO_3+H_2O \rightarrow \underset{\text{Basic zinc carbonate}}{ZnCO_3.Zn(OH)_2}$$

(vii) **Action of $NaHCO_3$ Solution** : Its solution gives zinc carbonate with $NaHCO_3$ solution.

$$\begin{array}{c} ZnSO_4+NaHCO_3 \rightarrow ZnCO_3+NaHSO_4 \\ NaHCO_3+NaHSO_4 \rightarrow Na_2SO_4+H_2O+CO_2 \\ \hline ZnSO_4+2NaHCO_3 \rightarrow ZnCO_3+Na_2SO_4+H_2O+CO_2 \end{array}$$

(viii) **Action of $MOH(M=Na, K)$** : $ZnSO_4$ solution gives sodium zincate, Na_2ZnO_2, with excess of $NaOH$ solution.

$$\begin{array}{c} ZnSO_4+2NaOH \rightarrow Zn(OH)_2+Na_2SO_4 \\ Zn(OH)_2+4NaOH \rightarrow Na_2ZnO_2+2H_2O \\ \hline ZnSO_4+4NaOH \rightarrow Na_2ZnO_2+Na_2SO_4+2H_2O \end{array}$$

(ix) Action of NH_4OH : When excess of NH_4OH is added to zinc sulphate solution then complex compound is obtained.

$$ZnSO_4+2NH_4OH \rightarrow Zn(OH)_2+(NH_4)_2SO_4$$

$$ZnSO_4+4NH_4OH \rightarrow \underset{\text{Zinc tetrammonium sulphate.}}{Zn(NH_3)_4SO_4}+4H_2O$$

Uses :

(i) As eye lotion and in other such medicine, (ii) In making lithopone ($BaSO_4+ZnS$), (iii) In preserving hides and woods, (iv) As a mordant in calico printing.

7. Lithopone ($BaSO_4+ZnS$) :

It is prepared by heating a mixture of $ZnSO_4$ and BaS.

$$ZnSO_4+BaS \rightarrow \underbrace{ZnS+BaSO_4}_{\text{Lithopone.}}$$

It is extensively used as a white pigment in paints because H_2S has got no effect on this.

8. Zinc Sulphide, ZnS :

Preparation : It occurs in nature as zinc blend. It may be prepared as follows—

(i) By the action of H_2S on vapours of zinc.

(ii) By heating zinc oxide with sulphur.

(iii) By adding ammonium sulphide on a solution of $ZnSO_4$.

$$ZnSO_4+(NH_4)_2S \rightarrow ZnS+(NH_4)_2SO_4.$$

(iv) By passing H_2S in ammonical medium over $ZnSO_4$ solution.

$$ZnSO_4+H_2S \rightarrow ZnS+H_2SO_4$$

Properties :

It is a white solid, but soluble in acids and alkalies.

$$ZnS+H_2SO_4 \rightarrow ZnSO_4+H_2S.$$

In presence of traces of impurities of these sulphides of Cu, Mn, Bi, Pb etc. it exhibits **phosphorescence.**

Uses : (i) In making luminous paints of the doals of watches, clocks etc. It consists of zinc sulphide with traces of a radium salt.

(ii) It is used in X-ray screens, in radioactive work and phosphorescent screens.

Analytical Tests for Zinc Salts :

(i) **Cobalt-Nitrate Test.** Zinc compounds when heated in a charcoal cavity, leave an incrustation of the metallic oxide, which is yellow when hot and white when cold. Moisten the incrustation with a drop of cobalt nitrate solution and heated, a green mass called *Rinnmann's Green* $CoO.ZnO$. is obtained.

$$ZnSO_4 \rightarrow ZnO + CO_2$$
$$2Co(NO_3)_2 \rightarrow 2CoO + 4NO_2 + O_2$$
$$CoO + ZnO \rightarrow CoO.ZnO \text{ (green).}$$

(ii) To $Zn^{+2}ZOn$ solution, NH_4Cl, NH_4OH are added followed by H_2S white precipitate of ZnS .

$$ZnSO_4 + H_2S \rightarrow ZnS + H_2SO_4$$

9. Galvanisation :

The process of covering iron sheets with a thin coat of zinc is known as galvansatoin and the iron sheet so obtained is known as **galvanised iron sheet.** This affords thc protection to iron from rusting. It does not permit water to come in contact with iron. In case a portion of zinc gets detached and iron surface is exposed, the iron will not rust, as it will form a galvanic couple with zinc which being more electropositive will itself pass into solution.

Galvanised iron can be obtained by first cleansing it with dil. H_2SO_4 or by sand, blasting and then dipping into a bath of molten zinc. The galvanised sheet is then passed through rollers in order to have a uniform coating.

Galvanised iron is very widely used for making useful articles like water buckets, gutters, tube, pipes etc.

16.4. Mercury

Symbol-Hg; *At. No.* 80 *At. Wt.* 200·59

Electronic Configuration : $1s^2$, $2s^2 2p^6$, $3s^2 3p^6 3d^{10}$, $4s^2 4p^6 4d^{10}$, $4f^{14}$, $5s^2 5p^6 5d^{10}$, $6s^2$.

Occurrence : The chief source of mercury is Cinnabar, HgS, which is found in Spain, Italy, Austria and California.

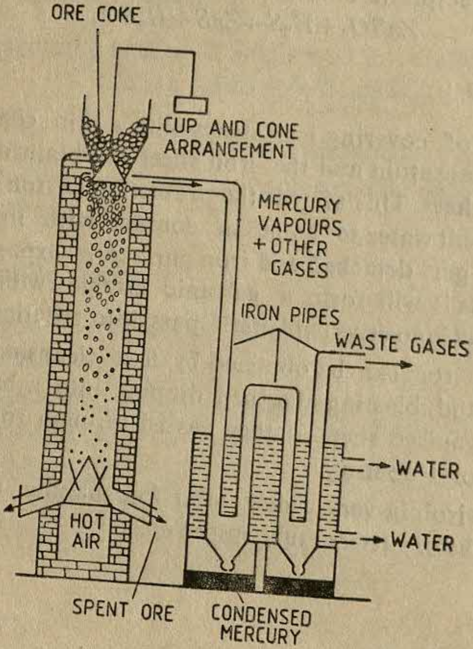
Extraction : Mercury is obtained from cinnabar, by a process of combined roasting and distillation :

$$HgS + O_2 \rightarrow Hg + SO_2$$

Various types of furnace have been used for this purpose. The most important of them are :

(a) **Idrian Furnace** : The ore is placed on perforated arches in the central chamber over the fire place. The ore on roasting gives off gases and mercury vapour. The gases, together with mercury vapour, pass through a series of chambers, in which the vapour of mercury condense.

(b) **Shaft Furnace** : This is used in the **modern process**. The furnaces work continuously. It is economical and suitable even for poor types of ores. The powdered ore is mixed with charcoal and dropped in the shaft furnace by a cup and conc. arrangement.

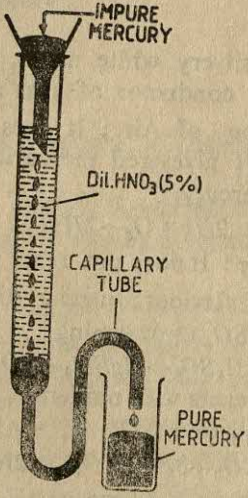


The furnace is heated to dull redness. Hot gases are made to pass in a counter current movement to the air. Gases with mercury vapours pass through iron pipes and led into water cooled condensers (See fig). The spent ore is withdrawn from the bottom and the furnance again fed with the charge as before.

Purification : The commercial mercury contains impurities of base metals like *Cd* and *Zn*. Purification of the commercial metal is carried out by any one of the two methods given below :

(a) By Vacuum Distillation : It is the best method for the purification of mercury. The distillation is carried out under reduced pressure.

(b) Treatment with Dil. HNO_3 and Mercurous Nitrate : For simple purification, commercial mercury is squeezed through linen or chamois leather and then gradually passed through 5% HNO_3 containing some $Hg_2(NO_3)_2$. It reacts with the dissolved metals forming their nitrates and liberating mercury. This process is repeated several times to get pure mercury.



COMPARISON BETWEEN Hg, Zn AND Cd,

Mercury Differs from Zn and Cd :

Differences :

(i) Much more noble than *Zn* and *Cd* in many respects. (ii) *Hg* is liquid at ordinary temp. while *Zn* and *Cd* are solids. (iii) *Hg* has a silver white lustre whereas *Zn* is bluish white and *Cd* is white metal. (iv) It has a higher specific gravity (13·46) than *Zn* (7·14) and *Cd* (8·64). (v) It is weakly electropositive and placed below hydrogen in the electrochemical series while *Zn* and *Cd* are strongly electropositive. (vi) It remains unfurnished in moist air. (vii) Its oxide is unstable and gives the metal on heating while *ZnO* and *CdO* are stable. (viii) It is not attacked by water or steam while Zn and Cd are slowly attacked by water. (ix) It is not attacked by dilute acids while Zn and Cd readily dissolve in dilute acids evolving hydrogen. (x) It forms two series of salts e.g. mercurous and mercuric while Zn and Cd form duly one series of compounds.

Properties :

Physical : (a) It is silvery white metal. (b) It is a liquid at R. T. P. (c) It is good conductor of heat and electricity.

Chemical : (i) **Action of Air :** It does not react with air at ordinary temperature. It gives red mercuric oxide when oxygen is passed over boiling mercury.

$$2Hg + O_2 \rightarrow 2HgO$$

(ii) **Action of Water :** It does not react with water.

(iii) **Action of Acids :** It does not react with dilute. HCl or H_2SO_4. It reacts with conc. H_2SO_4 on warming.

$$Hg + 2H_2SO_4 \rightarrow HgSO_4 + SO_2 + 2H_2O$$

to give mercurous. It reacts with moderate by HNO_3 to give mercurous nitrate $Hg_2(NO_3)_2$ and NO.

$$6Hg + 8HNO_3 \rightarrow 3Hg_2(NO_3)_2 + 2NO + 4H_2O.$$

It reacts with hot and conc. HNO_3 to give mercuric nitrate, NO and NO_2.

$$2Hg + 6HNO_3 \rightarrow 2Hg(NO_3)_2 + NO + NO_2 + 3H_2O$$

It reacts with aqua-regia to give $HgCl_2$.

$$HNO_3 + 3HCl \rightarrow NOCl + 2H_2O + 2Cl$$

$$Hg + 2Cl \rightarrow HgCl_2$$

(iv) **Action of Alkalies :** It does not react with alkalies.

(v) **Action of Halogen :** (a) When Cl_2 is passed over mercury then $HgCl_2$ is obtained.

$$Hg + Cl_2 \rightarrow HgCl_2$$

(b) When bromine (Br_2) vapour is passed over heated Hg then $HgBr_2$ is obtained.

$$Hg + Br_2 \rightarrow HgBr_2$$

(c) $$Hg + I_2 \xrightarrow[\text{in motor pestle}]{\text{rubbed}} HgI_2.$$

(vi) **Reaction with Metals :** It reacts with different metals to form amalgam.

$$NaHg_2;\ KHg_2;\ AuHg;\ MgHg_2 \text{ etc.}$$

Uses :

(a) Thermometer, Barometer, (b) Collection of gas, (c) Preparation of amalgam, (d) Extraction of *Ag* and *Au*, (e) Castner Kellner's Process.

16.5 Compounds of Mercury :

1. Mercuric Oxide, HgO :

Preparation : (i) It is prepared by heating mercury in air or oxygen.

$$2Hg+O_2\rightarrow 2HgO$$

(ii) It can be prepared by heating a mixture of $Hg_2(NO_3)_2$ and Hg at low temperature.

$$Hg_2(NO_3)_2+Hg\rightarrow 2HgO+2NO_2$$

(iii) When $NaOH$ solution is boiled with $HgCl_2$ or $Hg(NO_3)_2$ then yellow anhydrous HgO is precipitated out.

$$HgCl_2+2NaOH\rightarrow HgO+H_2O+2NaCl$$
$$Hg(NO_3)_2+2NaOH\rightarrow HgO+H_2O+2NaNO_3$$

When yellow HgO is heated to 300°C then red HgO is formed.

Properties :

(i) It is insoluble in water.

(ii) Yellow HgO is converted to red HgO at 300°C. It is converted into black HgO when strongly heated. According to ostwald the change in colour is due to change in the size of the particles of HgO.

$$\underset{\text{(Yellow)}}{HgO}\xrightarrow{300°C}\underset{\text{(Red)}}{HgO}\xrightarrow{\text{Strong}}\underset{\text{(Black)}}{HgO}\xrightarrow{\text{heat}}Hg+\tfrac{1}{2}O_2$$

(iii) It reacts with acids to give salts and water.

$$HgO+2HCl\rightarrow HgCl_2+H_2O.$$
$$HgO+H_2SO_4\rightarrow HgSO_4+H_2O.$$

(iv) When KI solution is added to suspension of HgO in water then mixture of potassium mercury iodide and KOH is obtained.

$$HgO+4KI+H_2O\rightarrow K_2[HgI_4]+2KOH$$

Uses : It is used as red dye.

2. Mercuric Sulphate, $HgSO_4$:

Preparation : (i) It is prepared by heating a mixture containing two parts of *Hg* and three parts of conc. H_2SO_4.

$$Hg+2H_2SO_4 \rightarrow HgSO_4+SO_2+2H_2O.$$

The solution on crystallisation gives crystal of $HgSO_4$.

(ii) It is prepared by the action of conc. H_2SO_4 on HgO,

$$HgO+H_2SO_4 \rightarrow HgSO_4+H_2O$$

Properties :

(i) It is white crystalline solid.

(ii) It decomposes on heating to give Hg_2SO_4 (ous), Hg, SO_2 and O_2.

$$3HgSO_4 \rightarrow Hg_2SO_4+Hg+2SO_2\uparrow+2O_2\uparrow$$

Uses : (i) In organic chemistry as catalyst.

(ii) In the preparation of mercurous and mercuric chloride.

3. Mercuric Nitrate $Hg(NO_3)_2\,2H_2O$:

Preparation : It is prepared by heating Hg or $Hg_2(NO_3)_2$ (ous) with conc. HNO_3.

$$2Hg+6HNO_3 \rightarrow 2Hg(NO_3)_2+NO+NO_2+3H_2O.$$

Properties :

(i) It is a colourless solid. (ii) It is soluble in water.

(iii) It is hydrolysed by excess of water to give basic nitrate.

$$Hg(NO_3)_2+H_2O \rightarrow HgOH.NO_3+HNO_3.$$

(iv) It decomposes on heating to give HgO, NO_2 and O_2.

$$2Hg(NO_3)_2 \rightarrow 2HgO+4NO_2+O_2.$$

Solution

(v) It reacts with $NaOH$ to give yellow precipitate of HgO.

$$Hg(NO_3)_2+2NaOH \rightarrow HgO+2NaNO_3+H_2O.$$

Uses : As laboratory reagent.

4. Corrosive Sublimate, $HgCl_2$ (Mercuric chloride)

Preparation : (i) It is prepared by passing chlorine over heated mercury.

$$Hg+Cl_2 \rightarrow HgCl_2.$$

(ii) It is prepared by the action of aqua-regia on mercury or mercurous chloride.

(a) $$\begin{array}{c} 3HCl+HNO_3 \rightarrow NOCl+2H_2O+2Cl \\ Hg+2Cl \rightarrow HgCl_2 \\ \hline Hg+3HCl+HNO_3 \rightarrow HgCl_2+NOCl+2H_2O \end{array}$$

(b) $$\begin{array}{c} 3HCl+HNO_3 \rightarrow NOCl+2H_2O+2\text{'}Cl\text{'} \\ Hg_2Cl_2+2Cl \rightarrow 2HgCl_2. \end{array}$$

(iii) It is also prepared by heating an equimolar mixture of mercuric sulphate and sodium chloride in a long necked flask in presence of little MnO_2, which acts as oxidising agent and prevents the formation of mercurous chloride (**commercial**).

$$HgSO_4+2NaCl \rightarrow HgCl_2+Na_2SO_4$$

Mercuric chloride sublimes and condenses on the upper part.

Properties :

(i) It is colourless, crystalline solid, fairly soluble in water, but more in alcohol and ether. It behaves like a covalent compound.

(ii) **As an Oxidising Agent** : It acts as an oxidising agent because it gains electron during chemical reaction.

$$2Hg^{++}+2e \rightarrow Hg_2^{++}$$

(a) Reaction with stannous chloride (r.a.)

(i) **Little $SnCl_2$** : $$\begin{array}{c} 2Hg^{++}+2e \rightarrow Hg_2^{++} \\ Sn^{++} \rightarrow Sn^{++++}+2e \\ \hline 2Hg^{2+}+Sn^{2+} \rightarrow Sn^{4+}+Hg_2^{2+} \end{array}$$

or $$2HgCl_2+SnCl_2 \rightarrow SnCl_4+Hg_2Cl_2.$$

(ii) **Excess $SnCl_2$** : $$\begin{array}{c} Hg^{++}+2e \rightarrow Hg \\ Sn^{++} \rightarrow Sn^{4+}+2e \\ \hline Hg^{++}+Sn^{++} \rightarrow Sn^{4+}+Hg. \end{array}$$

or $$HgCl_2+SnCl_2 \rightarrow SnCl_4+Hg.$$

(b) **Reaction with Sulphur Dioxide** (SO_2) : When SO_2 is passed into mercuric chloride solution then white precipitate of mercurous chloride (Hg_2Cl_2) is obtained.

$$\begin{array}{c} SO_2+2H_2O \rightarrow H_2SO_4+2\text{'}H\text{'} \\ 2HgCl_2+2\text{'}H\text{'} \rightarrow Hg_2Cl_2+2HCl \\ \hline 2HgCl_2+SO_2+2H_2O \rightarrow Hg_2Cl_2+H_2SO_4+2HCl \\ (2Hg^{++}+SO_2+2H_2O \rightarrow Hg_2^{++}+SO_4^{-2}+4H^+) \end{array}$$

In this reaction mercuric chloride is reduced to mercurous chloride. Hence it acts as an oxidising agent.

(iii) **Reaction with** *MOH* (*M*=*Na*, *K*) : When *NaOH* is added to mercuric chloride solution then yellow precipitate of mercuric oxide is formed.

$$HgCl_2+2NaOH \rightarrow HgO+2NaCl+H_2O.$$

(iv) **Reaction with Potassium Iodide** (KI) : When KI solution is added to mercuric chloride solution, first of all yellow precipitate of (HgI_2) is obtained. This is soluble in excess of KI solution giving potassium mercuric tetra iodide, $K_2[HgI_4]$. The alkaline solution of this is known as **Nessler's Reagent.**

(a) Little KI and excess of $HgCl_2$.

$$HgCl_2+2KI \rightarrow HgI_2+2KCl$$

(b) Excess KI and little of $HgCl_2$.

$$HgCl_2+4KI \rightarrow K_2\,[HgI_4].$$

(v) **Reaction with Ammonia :** It reacts with ammonia to give white precipitate of aminobasic mercuric chloride.

$$HgCl_2+2NH_3 \rightarrow HgNH_2Cl+NH_4Cl$$

(vi) **Reaction with H_2S :** When H_2S is passed into solution of mercuric chloride then black precipitate of HgS is obtained.

$$HgCl_2+H_2S \rightarrow HgS+2HCl$$

(vii) **Reaction with Na_2CO_3 :** When Na_2CO_3 solution is added to mercuric chloride solution then yellow precipitate of mercuric oxide (HgO) is obtained.

$$HgCl_2+Na_2CO_3 \rightarrow HgO+2NaCl+CO_2\uparrow$$

(viii) **Reaction with Hg :** When $HgCl_2$ is rubbed with Hg and heated then Hg_2Cl_2 is obtained.

$$HgCl_2+Hg \rightarrow Hg_2Cl_2$$

(ix) It is highly poisonous. Its antidote is white portion of egg.

Uses : (i) As antiseptic, (ii) In sterlisation of surgical instruments and for preservation of skin and furs.

5. Mercuric Sulphide (HgS) (Vermillion) :

Preparation : (i) When mercury is rubbed in a mortar pestle with flower of sulphur in presence of KOH (little) HgS is obtained. It is converted into red compound from black by sublimation. It is washed with water and dried.

$$Hg+S \rightarrow HgS$$

(ii) When H_2S is passed into mercuric chloride solution then black precipitate of HgS is obtained.

$$HgCl_2+H_2S \rightarrow HgS+2HCl$$

It is converted into red by heating

$$\underset{\text{Black}}{HgS} \rightarrow \underset{\text{Red}}{HgS}$$

Properties :

(i) It is red crystalline solid. (ii) It is very Sparingly soluble in water and acids.

(iii) Reaction with mod. HNO_3 : It reacts with HNO_3 to give $Hg(NO_3)_2$ and S.

$$\begin{array}{l} HgS+2HNO_3 \rightarrow Hg(NO_3)_2+H_2S \\ 3H_2S+2HNO_3 \rightarrow 4H_2O+2NO+3S \\ \hline 3HgS+8HNO_3 \rightarrow 3Hg(NO_3)_2+4H_2O+2NO+3S \end{array}$$

(iv) Reaction with Aqua Regia : It forms soluble $HgCl_2$ and S

$$\begin{array}{l} 3HCl+HNO_3 \rightarrow 2H_2O+NOCl+2\text{‘}Cl\text{’} \\ HgS+2\text{‘}Cl\text{’} \rightarrow HgCl_2+S \\ \hline HgS+3HCl+HNO_3 \rightarrow 2H_2O+NOCl+HgCl_2+S \end{array}$$

Uses : (i) In medicine. (ii) As red dye.

MERCUROUS COMPOUNDS

6. Mercurous Oxide, Hg_2O :

Preparation : When caustic soda solution is added in excess to a solution of mercurous nitrate a blackish brown precipitate of mercurous oxide is obtained.

$$Hg_2(NO_3)_2+2NaOH \rightarrow Hg_2O+2NaNO_3+H_2O$$

Properties :

(i) It is blackish brown powder, sparingly soluble in water.

(ii) It is unstable and it decomposes when exposed to light.

$$Hg_2O \rightarrow Hg+HgO$$

On heating in air it forms mercuric oxide.

$$2Hg_2O+O_2 \rightarrow 4HgO.$$

7. Mercurous Nitrate, $Hg_2(NO_3)_2 \cdot 2H_2O$:

Preparation : (i) It is formed by the action of cold and dilute nitric acid on an excess of mercury, the clear solution is evaporated to crystallisation.

$$6Hg+8HNO_3 \rightarrow 3Hg_2(NO_3)_2+2NO+4H_2O.$$

Properties :

(i) It is white crystalline substance, soluble in water.

(ii) In contact with excess of water the crystals give a white precipitate of basic nitrate which is soluble in water.

$$2Hg_2(NO_3)_2+2H_2O \rightarrow Hg_2(NO_3)_2.Hg_2O.H_2O+2HNO_3$$

(iii) It forms a white precipitate of mecurous chloride with dil. HCl.

$$Hg_2(NO_3)_2+2HCl \rightarrow Hg_2Cl_2+2HNO_3$$

(iv) It forms a white precipitate of mercurous sulphate with dil. H_2SO_4.

$$Hg_2(NO_3)_2+H_2SO_4 \rightarrow Hg_2SO_4+2HNO_3$$

(v) On heating it decomposes as follows—

$$Hg_2(NO_3)_2 \rightarrow 2HgO+2NO_2$$
$$2HgO \rightarrow 2Hg+O_2.$$

8. Mercurous Sulphate, Hg_2SO_4 :

Preparation : (i) It is obtained as a white precipitate when a soluble sulphate or dil. H_2SO_4 is added to mercurous salt solution.

$$Hg_2(NO_3)_2+H_2SO_4 \rightarrow 2HNO_3+Hg_2SO_4$$

(ii) It is also obtained by the action of sulphuric acid on an excess of mercury.

$$2Hg+2H_2SO_4 \rightarrow Hg_2SO_4+2H_2O+SO_2\uparrow$$

Properties :

(i) It is white solid sparingly soluble in water.

(ii) It is hydrolysed by water to give greenish yellow colour of basic salt.

$$2Hg_2SO_4+2H_2O \rightarrow Hg_2SO_4.Hg_2O.H_2O+H_2SO_4$$

Uses : In the standard **weston Cadmium.**

9. Calomel, Hg_2Cl_2, or $Cl^- - Hg^+ - Hg^+ - Cl^-$:

Preparation : (i) It is prepared by the action of dilute HCl on mercurous nitrate solution.

$$Hg_2(NO_3)_2+2HCl \rightarrow \underset{\text{white}}{Hg_2Cl_2}\downarrow+2HNO_3$$

(ii) It is prepared on the large scale by heating a mixture of $HgCl_2$ (ic) and Hg in a closed vessel, when Hg_2Cl_2 formed sublimes off and condenses as a white solid.

$$HgCl_2+Hg \rightarrow Hg_2Cl_2$$

It is repeatedly washed with dil. HNO_3 to remove mercury and with boiling water to remove mercuric chloride.

(iii) It is prepared by passing SO_2 to mercuric chloride ($HgCl_2$) solution.

$$\begin{array}{c} SO_2+2H_2O \rightarrow H_2SO_4+2\text{'}H\text{'} \\ 2HgCl_2+2\text{'}H\text{'} \rightarrow Hg_2Cl_2+2HCl \\ \hline 2HgCl_2+SO_2+2H_2O \rightarrow Hg_2Cl_2+H_2SO_4+2HCl. \end{array}$$

Properties :

(i) It is white amorphous powder, insoluble in water and dilute acids.

(ii) **Action of Heat :** It dissociates to Hg and $HgCl_2$.

$$Hg_2Cl_2 \rightarrow Hg+HgCl_2.$$

(iii) **Action of Aqua Regia :** It converts it into soluble mercuric chloride.

$$\begin{array}{c} 3HCl+HNO_3 \rightarrow NOCl+2H_2O+2Cl \\ Hg_2Cl_2+2Cl \rightarrow 2HgCl_2 \\ \hline Hg_2Cl_2+3HCl+HNO_3 \rightarrow 2HgCl_2+NOCl+2H_2O. \end{array}$$

(iv) **Action of Ammonia :** It turns black forming a mixture of aminobasic mercuric chloride and finely divided mercury.

$$Hg_2Cl_2+2NH_4OH \rightarrow \underbrace{Hg+HgNH_2Cl}_{\text{Black}}+NH_4Cl+2H_2O$$

(v) **Action of $NaOH$:** It gives grey precipitate of mercurous oxide

$$Hg_2Cl_2+2NaOH \rightarrow Hg_2O+2NaCl+H_2O.$$

Uses : (i) As a purgative in medicine, (ii) As electrode.

Typical Questions With Answer

1. Pure Zinc does not give hydrogen with dilute acids.

Ans. : Zinc is above hydrogen in electrochemical series but pure zinc has very little action with dil. acids owing to the over-potential of hydrogen at the zinc surface.

2. Mercury is stored in iron bottles. Explain in two to three lines.

Ans. : Mercury forms alloys called **amalgams** with almost all metals but iron does not form alloy with mercury. Hence it can be stored in iron bottles.

3. How would you bring about the following conversions ?

(i) Calomel into corrosive sublimate and vice versa.

(ii) Mercury to (a) calomel, (b) corrosive sublimate, (c) vermillion, (d) Nessler's reagent.

(iii) White vitriol to zinc carbonate.

(iv) Zinc carbonate to anhydrous zinc chloride.

Ans. : (i) *Calomel* (Hg_2Cl_2) *into corrosive sublimate* ($HgCl_2$)

When calomel is treated with aqua regia then corrosive sublimate is obtained.

$$3HCl + HNO_3 \rightarrow NOCl + 2Cl + 2H_2O$$

$$\underset{\text{calomel}}{Hg_2Cl_2} + 2Cl \rightarrow \underset{\text{corrosive sublimate.}}{2HgCl_2}$$

Corrosive sublimate to calomel :

By grinding corrosive sublimate with mercury followed by sublimation. The sublimate is washed with water to remove any mercuric chloride.

$$HgCl_2 + Hg \rightarrow Hg_2Cl_2.$$

(ii) (a) *Mercury to calomel* (Hg_2Cl_2) *:*

When mercury (in excess) is treated with dilute nitric acid mercurous nitrate is formed.

$$6Hg + 8HNO_3 \rightarrow 3Hg_2(NO_3)_2 + 2NO + 4H_2O$$

On treatment with hydrochloric acid, mercurous nitrate forms mercurous chloride (calomel)

$$Hg_2(NO_3)_2 + 2HCl \rightarrow 2HNO_3 + \underset{\text{white}}{Hg_2Cl_2}$$

(b) *Mercury to corrosive sublimate* ($HgCl_2$) *:*

$HgCl_2$ is obtained on heating Hg with Cl_2 gas.

$$Hg + Cl_2 \rightarrow HgCl_2$$

(c) *Mercury to vermillion* (HgS) *:*

By rubbing mercury and sulphur with a little $NaOH$ or KOH solution, when the black sulphide first formed gradually turns red crystalline i.e. vermillion.

$$Hg + S \rightarrow HgS \text{ (red)}$$

(d) *Mercury to Nessler's reagent :*

By rubbing mercury with requisite quantity of iodine in presence of alcohols mercuric iodide is formed :

$$Hg + I_2 \rightarrow HgI_2$$

Mercuric iodide dissolves in excess of KI.

$$HgI_2 + 2KI \rightarrow K_2[HgI_4]$$

The aqueous solution of $K_2[HgI_4]$ is KOH is known as the *Nessler's reagent.*

(iii) When white vitriol solution is boiled with $NaHCO_3$ solution then zinc carbonate is obtained.

$$ZnSO_4 + 2NaHCO_3 \rightarrow ZnCO_3 + Na_2SO_4 + H_2O + CO_2 \uparrow$$

(iv) When zinc carbonate is treated with dilute. HCl then $ZnCl_2$ in solution is obtained. This on crystallisation gives $ZnCl_2.2H_2O$. This on treatment with NH_4Cl geven a double salt. This is heated in a current of dry HCl gas to given anhydrous $ZnCl_2$

$$ZnCO_3 + 2HCl \rightarrow ZnCl_2 + H_2O + CO_2.$$

$$ZnCl_2 + NH_4Cl \rightarrow ZnCl._2NH_4Cl$$

$$ZnCl_2.NH_4Cl \xrightarrow[\text{gas (heat)}]{HCl} ZnCl_2 + NH_4Cl.$$

4. Explain the following :

(i) Zinc dust is more reactive than zinc granules.

(ii) Zinc oxide becomes yellow when heated but returns to its original white colour on cooling.

(iii) Addition of zinc granules to $CuSO_4$ solution decolourizes it.

(iv) Zinc hydroxide dissolves in both NH_4OH and $NaOH$ solutions but copper hydroxide dissolves only in NH_4OH.

Ans. (i) The reactivity depends upon the surface area. Since zinc dust has more surface area than granulated zinc, hence zinc dust is more reactive than granulated zinc.

(ii) When zinc oxide is heated, a little oxygen is lost reversibly. This leaves a non-stoichio-metric compound. The crystal lattice is distributed in such a way that electrons from the excess zinc metal remaining, can move in the crystal almost as freely as they can in a metal. This makes zinc oxide a semi-conductor and gives it a yellow colour which is lost when oxygen is taken up again an cooling, it gives with zinc oxide.

(iii) Zinc displaces copper from copper sulphate solution (blue) forming $ZnSO_4$ (colourless solution).

$$\underset{\text{Blue}}{Zn + CuSO_4} \rightarrow \underset{\text{colourless}}{ZnSO_4} + Cu \downarrow$$

Hence zinc decolourises $CuSO_4$ solution.

(iv) Zinc hydroxide dissolves in $NaOH$ and NH_4OH both forming the soluble sodium salt and soluble zinc ammino complex.

$$Zn(OH)_2 + 2NaOH \rightarrow Na_2ZnO_2 + 2H_2O$$

$$Zn(OH)_2 + 4HN_4OH \rightarrow 6[Zn(NH_3)_4](OH)_2.$$

Copper hydroxide does not form zincate like soluble compounds with $NaOH$, but it dissolves in ammonia forming a soluble complex giving a deep blue solution.

$$Cu(OH)_2+4NH_3 \rightarrow \underset{\text{Tetrammino copper (II) hydroxide.}}{[Cu(NH_3)_4](OH)_2}$$

5. How will you distinguish between mercurous chloride (calomel, Hg_2Cl_2) and mercuric chloride (corrosive sublimate, $HgCl_2$).

Ans. :

Tests	Hg_2Cl_2	$HgCl_2$
(i) Solubility in water	Insoluble in water	Fairly soluble in water.
(ii) $SnCl_2$	Grey black ppt. $SnCl_2+Hg_2Cl_2 \rightarrow \underset{\text{Black}}{2Hg\downarrow}+SnCl_4$	Given white ppt. and then turm a grey black ppt. $2HgCl_2+SnCl_2 \rightarrow \underset{\text{White}}{Hg_2Cl_2\downarrow}+SnCl_4$ $Hg_2Cl_2+SnCl_2 \rightarrow \underset{\text{Black}}{2Hg}+SnCl_4$
(iii) With NH_3	Turns black $Hg_2Cl_2+2HN_3 \rightarrow \underbrace{Hg+Hg(NH_2)Cl_2\downarrow}_{\text{Black}}$	Gives white ppt. $HgCl_2+2NH_3 \rightarrow \underset{\text{white}}{Hg(NH_2)Cl}+NH_4Cl$
(iv) Action of $NaOH$	Black ppt. of $HgO+Hg_2O+Hg$	Yellow ppt. of HgO.

QUESTIONS

Long and Short Type :

1. Discuss the position of Zn, Cd and Hg in the periodic table.

2. Describe the extraction of zinc from its sulphide ore (zinc blende). How it is purified ?

What is the action of following reagent on zinc.

(a) conc. H_2SO_4, (b) hot caustic potash solution, (c) HNO_3.

3. Write the names and formulae of the chief ore of Mercury. How is Hg obtained from this ore ?

Describe the purification of Hg.

How will you obtain the following from Hg.

(a) Calomel, (b) corrosive sublimate.

(M.U. 1968; Bhag.U. '68; B.U. '69; P.U. '78)

4. Write notes on

(a) corrosive sublimate, (b) Calomel, (c) Galvanising, (d) Nessler's reagent, (e) White vitriol, (f) Vermillion, (g) Nessler's Reagent.

5. What happens when

(a) Cu reacts with $HgCl_2$, (b) KI reacts with $HgCl_2$ **(P.U. 1976; I.I.T. '78)** (c) Caustic Soda solution is added to white vitriol **(P.U. 1976)**, (d) NH_4OH is added to white vitriol, (e) Zn is boiled with conc. $NaOH$ solution, (f) $SnCl_2$ is added to $HgCl_2$ **(P.U. 1976; M.U. '78; I.I.T. '77, '79)**, (g) H_2S is passed in $ZnSO_4$ solution made alkaline with NH_4Cl and NH_4OH, (h) Hg_2Cl_2 reacts with NH_4OH **(I.I.T. 1979)**.

(i) Hg reacts with aqua regia.

6. How will you detect the presence of—

(a) Mercuric chloride in calomel **(P.U. 1976)**, (b) Zinc in zinc dust **(P.U. 1976)**,
(c) Zinc in $ZnSO_4.7H_2$. **(P.U. 1976)**

7. Cpmplete and balance the following reactions—

(a) $3HgS+12HCl+2HNO_3 \rightarrow 3H_2HgCl_4+NO+\ldots+4H_2O$ **(I.I.T. 1966)**
(b) $Zn+NaNO_3+NaOH \rightarrow Na_2ZnO_2+NH_3+H_2O$ **(I.I.T. 1966)**
(c) $Zn+HNO_3$ (dil.)$\rightarrow \ldots\ldots+\ldots\ldots+N_2O$ **(I.I.T. 1969)**
(d) $Zn+NaOH \rightarrow Na_2ZnO_2+\ldots\ldots$
(e) $HgCl_2+SnCl_2 \rightarrow Hg_2Cl_2+\ldots\ldots$
(f) $HgCl_2+KI \rightarrow K_2HgI_4+\ldots\ldots$
(g) $HgCl_2+H_2S \rightarrow \ldots\ldots+\ldots\ldots$
(h) $ZnSO_4+K_4[Fe(CN)_6] \rightarrow \ldots\ldots+\ldots\ldots+\ldots\ldots$ **(I.I.T. 1977)**

8. Discuss the Principles involved in the extraction and purification of mercury from cinnabon. How would you convert mercuric chloride from mercurous chloride and vice versa ? **(BICE 1984)**

9. Give reasons for the following—

(a) Addition of Zn granules to $CuSO_4$ solution decolourises it. **(I.I.T. 1967)**
(b) Zn dust is more reactive than zinc granules. **(I.I.T. 1971)**
(c) $ZnSO_4.7H_2O$ dissolves in $NaOH$ solution but $CuSO_4.5H_2O$ does not. **(I.I.T. 1975)**
(d) ZnO is used for making white paint. **(I.I.T. 1972)**
(e) $Hg(NO_3)_2$ on heating yields Hg and not HgO.
(f) Valency of Mercury is 1 and 2.

Short Questions Type :

10. The element Zn belongs to IIB group of the periodic table but it does not exhibit variable valency. Why ?

11. What is the general electronic configuration of IIB group elements ?

12. Fill up the blanks—

(a) The elements Zn, Cd and Hg are present in group........of the periodic table.
(b) Hg is a.........at ordinary temperature.
(c) White Vitriol has the formula..........
(d) Nessler's reagent is used for detecting..........

(e) The compound.........is known as philospher's wool.

(f) The alloys of mercury with other metals are called..........

13. Write down the chemical formule of the following—

(i) Calamine, (ii) Calomel, (iii) Philospher's wool, (iv) White vitriol, (v) Nessler's reagent, (vi) Vermillion, (vii) Chinese white, (viii) Reimann's green, (ix) corrosive sublimate, (x) Cinnabar, (xi) Lithopone, (xii) Zinc blende, (xiii) Willemite,

14. Describe the action of heat on the following—

(a) Calomel, (b) White vitriol, (c) Cinnabar, (d) Calamine, (e) Zinc in air, (f) Hg in air.

15. How would you obtain ?

(a) ZnS from a mixture of ZnS and Na_2ZnO_2.

(b) $HgCl_2$ from a mixture of $NaCl$ and Hg_2Cl_2.

(c) $ZnSO_4.7H_2O$ from a mixture of $ZnSO_4$ and $CuSO_4$.

16. Arrange the following according to the instructions given in the bracket—

(i) $ZnCO_3$, $CdCO_3$, $HgCO_3$ (in order of decreasing thermal stability).

(ii) Zn, Hg, Cd (in decreasing order of malleability and ductility)

(iii) Zn, Hg, Cd (in inereasing order of reactivity with chlorine).

(iv) ZnO, CdO, HgO (in order of decreasing thermal stability).

(v) $Zn(OH)_2$, $Cd(OH)_2$, $Hg(OH)_2$ (in order of decreasing thermal stability).

(vi) Zn, Cd, Hg (in order of increasing volatility).

(vii) Zn, Cd, Hg (in order of decreasing reactivity).

(viii) Zn, Cd, Hg (in order of increasing covalent bond formation).

(ix) Zn, Cd, Hg (in order of increasing complex formation).

(x) Zn, Cd, Hg (in order of increasing atomic size).

(xi) $ZnCl_2$, $CdCl_2$, $HgCl_2$ (in order of increasing volatility).

17. How will you distinguish between—

(a) $HgCl_2$ and Hg_2Cl_2, (b) $ZnSO_4$ and $CuSO_4$, (c) $Zn(NO_3)_2$ and $Hg(NO_3)_2$.

Select and write the correct answers from the following

18. Zinc reacts with dilute HNO_3 to give produces—
(1) NO, (2) NH_4NO_3, (3) NO_2, (4) H_2. **(N.C.E.R.T. 1974)**

19. Mercury is transported in metal containers made of
(1) Ag, (2) Pb, (3) Fe, (4) Al. **(C.P.M.T. 1973)**

20. If $NaOH$ is added to an aqueous solution of Zn^{++} ions, a white precipitate appears and on adding excess of $NaOH$, the ppt. dissolves. In this solution zinc exists in the

(1) Anionic part, (2) Cationic part, (3) Both in cationic and anionic part, (4) There is no zinc left in the solution. **(N.C.E.R.T. 1977)**

21. Cinnabar is an ore of.
(1) Hg, (2) Zn, (3) Zn, (4) Pb. **(C.I.M.T. 1978)**

22. Sulphide ore of zinc is concentrated by
(1) Floatation Process, (2) Electromagnetic Process, (3) Gravity separation, (4) Distillation. **(C.P.M.T. 1979)**

23. Which of the following is the weakest base ?
(1) $NaOH$, (2) KOH, (3) $Ca(OH)_2$, (4) $Zn(OH)_2$. **(I.I.T. 1980)**

24. Which of the following dissolves in hot concentrated solution of $NaOH$?
(1) Zn, (2) Fe, (3) Cu, (4) Ag. **(I.I.T. 1980)**

25. Galvanisation is the
(1) Deposition of zinc on iron, (2) Deposition of Al on Fe, (3) Deposition of tin on Fe, (4) Deposition of Cu of Fe. **(C.P.M.T. 1980)**

26. The important zinc ore is.
(1) Calamine, (2) Cryolite, (3) Cinnabar, (4) Malachite. **(C.P.M.T. 1980)**

27. Essential constituent of amalgam is
(1) An alkali, (2) Mercury, (3) Silver, (4) An alkali metal.

28. Normal zinc carbonate is prepared by treating an aqueous solution of a zinc salt with
(1) Na_2CO_3, (2) $NaHCO_3$, (3) CO_3, (4) K_2CO_3.

29. Brass is an alloy of
(1) Cu and Hg, (2) Cu and Zn, (3) Zn and Cd, (4) Cu and Cd.

30. Calamine is an ore of.
(1) Zn. (2) Cd, (3) Hg, (4) Cu.

31. The principal ore of Mercury from which metal is extracted is
(1) Calamine, (2) Calomel, (3) Cinnabar, (4) More than one.

32. Which of the following ore of zinc contains carbon ?
(1) Zinc blende, (2) Calamine, (3) Willemite (4) Zincite.

33. Which of the following is insoluble in water ?
(1) $ZnSO_4$, (2) Hg_2Cl_2, (3) $HgCl_2$, (4) $Zn(NO_3)_2$.

34. Which of the following is known as a Philospher's wool ?
(1) $ZnSO_4.7H_2O$, (2) ZnO, (3) $HgCl_2$, (4) Hg_2Cl_2.

35. Lithopone is a mixture of
(1) $ZnS+BaSO_4$, (2) $ZnSO_4$ and BaS, (3) ZnS and $ZnSO_4$, (4) BaS and $BaSO_4$.

36. On treatment with ammonia solution, corrosive sublimate forms a
(1) black ppt., (2) white ppt., (3) yellow ppt., (4) red ppt.

37. Sodium amalgam is an alloy of
(1) Na and Zn, (2) Zn and Hg, (3) Na and Hg, (4) Ag and Hg ?

38. Which of the following is isomorphous with white vitriol
(1) Vermillion, (2) Calomel, (3) corrosive sublimate, (4) Epsom Salt.

39. Which of the following is a liquid metal ?
(1) Zn, (2) Cd, (3) Hg, (4) Fe, (5) Na.

□□□

CHAPTER 17

ALUMINIUM

17.1. Aluminium

Symbol—*Al*. *At. No.* 13. *At. wt.* 26·98.
Electronic configuration : $1s^2 2s^2 2p^6 3s^2 3p^1$.

Occurrence : Aluminium is the most abundant metal in the earth's crust. Aluminium (also called, **aluminum** in U.S.A.) does not occur free in nature, but its compounds are numerous and widely distributed.

(i) **As aluminosilicates.** Clay, kaolin or (China clay), mica and feldspar.

(ii) **As anhydrous oxide** : Al_2O_3, occurs as **corundum** and **emerald.**

(iii) **As hydrated oxide : Bauxite,** $Al_2O_3.2H_2O$; **Diaspore**, $Al_2O_3\ H_2O$.

(iv) **As fluoroaluminate** : **Cryolite,** Na_3AlF_6 or $AlF_3.3NaF$.

Aluminium is profitably extracted from the ore **bauxite.** In India, bauxite is found in Bihar (Lohardaga), M.P., Orissa, J and K, Gujarat etc.

Extraction of Aluminium :

The chief and important ore from which aluminium is exclusively obtained is **Bauxite,** $Al_2O_3.2H_2O$. The extraction of the metal from it involves three main steps :

(A) Purification of Bauxite, (B) Electrolytic reduction of Alumina, (Al_2O_3), (C) Purification of Al.

(A) Purification of Bauxite :

Bauxite is either white or brown in colour depending upon the presence of too much, SiO_2; TiO_2 or Fe_2O_3 respectively. The purification is carried out as below :

(i) **Halls Dry Process :** Bauxite is fused with sodium carbonate. Sodium meta aluminate, $NaAlO_2$, is produced which is soluble in water. It is extracted with water. The impurities present viz. ferric oxide and silica, are left behind.

$$Al_2O_3 + Na_2CO_3 \rightarrow 2NaAlO_2 + CO_2$$

The water extract is heated to 50°-60°C and a current of carbon dioxide is passed through it. Aluminium hydroxide is precipitated and is ignited to obtain pure alumina.

$$2NaAlO_2+3H_2O+CO_2\rightarrow 2Al(OH)_3+Na_2CO_3$$
$$2Al(OH)_3\rightarrow Al_2O_3+3H_2O$$

(ii) **Baeyer's Process** (For ores containing much of Fe_2O_3) : The calcined bauxite is digested with strong $NaOH$ solution at 150° under pressure when alumina (Al_2O_3) dissolves out leaving behind oxides of iron, titanium as residue.

$$Al_2O_3+2NaOH\rightarrow \underset{\text{Sod. aluminate}}{2NaAlO_2}+H_2O$$

The mass is filtered and the filtrate is stirred with freshly precipitated $Al(OH)_3$. Sodium meta-aluminate in filtrate is hydrolysed and is changed into aluminium hydroxide which gets precipitated.

$$NaAlO_2+2H_2O\rightarrow Al(OH)_3\downarrow+NaOH$$

$$Al_2O_3+3H_2O+2OH^-\rightarrow 2Al(OH)_4^-\xrightarrow{2H^+}2Al(OH)_3+2H_2O$$

The precipitate is filtered off, washed, dried and heated to get pure alumina (rotary furnace).

$$2Al(OH)_3\xrightarrow{1500^\circ}Al_2O_2+3H_2O$$

(iii) **Serpeck's Process** (For ores contained much of silica, SiO_2) : The ore is heated with carbon at 1800°C and nitrogen is passed over it. Aluminium nitride is formed which on hydrolysis with water yields $Al(OH)_3$. This is separated and calcined to get alumina.

$$\underset{\text{Bauxite}}{Al_2O_3}+3C+N_2\rightarrow 2AlN+3CO\uparrow$$
$$AlN+3H_2O\rightarrow Al(OH)_3+NH_3\uparrow$$
$$2Al(OH)_3\rightarrow Al_2O_3+3H_2O$$
$$SiO_2+2C\rightarrow Si+2CO$$

Silica present as impurity is reduced by carbon to silicon which volatilises at the high temperature employed.

(B) **Electrulytic Reduction of pure Al_2O_3 (Hall and Heroult process, 1886) :**

Aluminium metal has great affinity for oxygen and thus the reduction of its oxide by carbon is not possible under ordinary conditions. It does not take place at very high temperature but the metal formed, reacts with carbon to form aluminium carbide (Al_4C_3).

$$Al_2O_3+3C=2Al+3CO\uparrow$$
$$4Al+3C=Al_4C_3$$

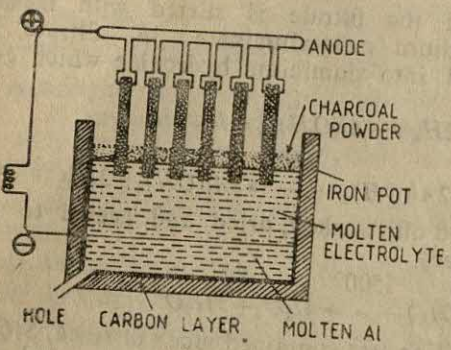
The reduction is however, possible electrolytically, but is confronted with the following difficulties :

(a) Pure Al_2O_3 is a bad conductor of electricity and has very high M.P. above 2000°C.

(ii) If electrolysis of fused alumina is carried out, metal aluminium formed will vaporise off as its b.p. is about 1800°C.

Principle of Extraction : Alumina is mixed with cryolite (Na_3AlF_3), fluorspar (CaF_2) in the ratio 20 : 60, whereby it not only becomes good conductor but also fuses at about 900°C which is much below the b.p. of aluminium.

The electrolysis of the fused mass is carried out in an iron box which is lined with gas carbon. The lining serves as the cathode, the anode consists of carbon rods dipped in the fused mass (see fig.). The fused electrolyte is kept covered with a layer of powdered coke to prevent any action of air. The voltage employed in the electrolysis is 5·3 volts. The current passed (about 50,000 amperes) serves two purposes (i) heating and (ii) electrolysis. Thus the fused mass is automatically kept at 900°C during electrolysis.



Aluminium is obtained at the cathode and being heavier than the electrolyte, sinks to the bottom and is tapped off periodically from the tap hole. Oxygen liberated at the anode attacks carbon rods and forms CO and CO_2. During electrolysis the concentration of the electrolyte goes on falling thereby increasing the resistance of the cell which is indicated by the glowing of a lamp placed parallel. Most of the alumina is then added and the process is made continuous.

The probable reactions may be given as :

$$4AlF_3 \rightarrow 4Al^{+3} + 12F^{-1}$$

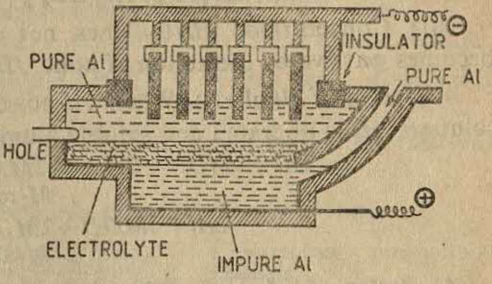
$$12F^- \rightarrow 12F + 12e^-$$

$$\left.\begin{array}{r} 2Al_2O_3 + 12F \rightarrow 4AlF_3 + 3O_2 \\ 4C + 3O_2 \rightarrow 2CO + 2CO_2 \end{array}\right] \text{At anode}$$

$$4Al^{+++} + 12e^- \rightarrow 4Al \quad \text{At cathode}$$

Purification : Aluminium as produced by the electrolysis of Al_2O_3 is 99% pure. It can be refined further up to 99·9% purity by **Hoope's Process.**

The electrolytic cell consists of an iron tank lined with carbon. It is filled with three liquids differing in specific gravity. The upper layer is of pure fused aluminium and serves as cathode.



The bottom layer is that of impure metal in the fused state and serves as anode. The central layer is that of molten mixture of the fluorides of *Al*, *Ba* and *Na* and serves as an electrolyte.

On passing electric current, pure aluminium goes to the top layer from the central layer and an equivalent amount of the metal from the bottom layer passes into the central layer. There is thus a gradual transference of aluminium from the bottom layer to the top and the impurities are left behind. Crude aluminium is added from time to time.

Properties of Aluminium :

Physical :

(i) It is a bluish white metal with a brilliant lustre. (ii) It is a light metal and its density is 2·7. (iii) Its m.p. and b.p. are 658·7°C and 1800°C respectively. (iv) It is good conductor of heat and electricity. (v) It forms alloys with other metals.

Chemical :

1. *Action of air* : It is not affected by dry air but in moist air a film of oxide is formed on the surface. It burns in oxygen producing oxide.

$$4Al+3O_2 \rightarrow 2Al_2O_3+77{\cdot}2 \text{ k cals.}$$
$$2Al+N_2 \rightarrow 2AlN$$

2. *Action of water* : Pure aluminium is not affected by pure water but impure metal is corroded by water containing some impurities.

It decomposes by boiling water evolving hydrogen.

$$2Al+6H_2O \rightarrow 2Al(OH)_3+3H_2$$

3. *Action of acids* : (i) Dil. HCl and H_2SO_4 produce hydrogen with *Al*.

$$2Al+6HCl \rightarrow 2AlCl_3+3H_2$$
$$2Al+3H_2SO_4 \rightarrow 2Al_2(SO_4)_3+3H_2$$

(ii) Hot and concentrated H_2SO_4 produces sulphur dioxide.

$$2Al+6H_2SO_4 \rightarrow Al_2(SO_4)_3+6H_2O+3SO_2$$

(iii) Concentrated HNO_3 does not react with Al because it becomes passive by the action of conc. HNO_3 due to Al_2O_3 layer.

4. *Action of alkalies* : When Al-powder is boiled with $NaOH$ solution, H_2 is liberated and soluble aluminates are formed.

$$2Al+2MOH+2H_2O \rightarrow \underset{M\text{-meta aluminate}}{2MAlO_2} + 3H_2$$

$$2Al+6MOH \rightarrow \underset{M\text{-aluminate}}{2M_3AlO_3} + 3H_2 \ (M=Na, K)$$

5. *Action of halogens* : When halogens are passed over heated aluminium then aluminium halides are formed.

$$2Al+3Cl_2 \rightarrow 2AlCl_3$$

6. *Action of nitrogen* : Aluminium when heated with nitrogen gives aluminium nitride.

$$2Al+N_2 \rightarrow 2AlN$$

7. *Displacement of other metals* : Aluminium displaces copper, zinc and lead from the solutions of their salts because these metals are less electropositive than Al.

$$3ZnSO_4+2Al \rightarrow Al_2(SO_4)_3+3Zn$$

Uses :

1. Aluminium, being very light, is used in household utensils, aeroplane parts, precision and surgical instruments etc.
2. Since it is unattacked by nitric acid, it is used in chemical plants and also for transporting nitric acid.
3. Aluminium foil is used for packing chocolates, cigarettes etc.
4. Alums are used as mordants in dyeing and paints.
5. Mixed with oil, it is used for steam pipes and other metal objects.
6. It is used as a reducing agent for the production of certain metals such as chromium, iron, manganese etc.
7. Alumina is used for making refractory bricks and ultramarine.
8. It is used in sizing of paper, along with organic colloids.
9. It is used in **Thermite welding** of metals.

Aluminium alloys : Aluminium forms a number of useful alloys which are as follows :

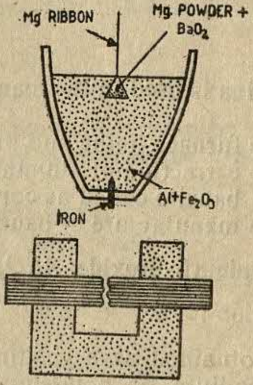
Alloys of Aluminium

Alloy	*Approximate composition*	*Uses*
(1) Aluminium bronze	Al 10%, Cu 90%	For hard, non-corrodible vessels
(2) Duraluminium	Al 95%, Cu 3%, Mn 1% Mg 1%	Aeroplanes and automobile parts
(3) Magnalium	Al 90%, Mg 10%	Balance beams
(4) γ-alloy	Al 92·5%, Cu 4%, Ni 2%, Mg 1·4%	Aeroplanes, non-corrodible vessels

17.2. Goldschmidts' Aluminothermic Process

The evolution of enormous quantities of heat in the oxidation of aluminium is used in **thermit welding** of metals. This process is also known as **Gold-schmidts' Aluminothermic Process.**

A mixture containing 3 parts of ferric oxide and one part of aluminium powder is placed in a crucible lined with magnesite and having a plug hole (see fig.). This is covered with a layer of mixture of magnesium powder and barium peroxide, with a magnesium ribbon inserted into it to act as a fuse. The broken ends of a rail or a girder etc. are brought nearer and thoroughly cleaned and surrounded by a fire-clay mould. When the magnesium ribbon fuse is ignited, the reaction



$$2Al+Fe_2O_3 \rightarrow Al_2O_3+2Fe$$
$$(H=-3230 \text{ kJ})$$

starts producing tremendous amount of heat as a result of which the iron melts. This white hot molten iron is tapped from the crucible into the mould. The heated ends of the iron rods (to be welded) actually melt and mix with the molten metal added, giving a firm and strong weld.

17.3. Compounds of Aluminium

1. Aluminium oxide, Alumina, Al_2O_3 **:** It is the most stable compound of aluminium. It occurs in nature as colourless corrundum and in combination with different metallic oxides as saphire, ruby, emery, amethyst, etc.

Preparation :

(i) It is prepared by heating aluminium hydroxide.

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

(ii) On burning aluminium in air.

$$4Al + 3O_2 \rightarrow 2Al_2O_3$$

Properties :

1. It is white solid substance, insoluble in water.

2. It is an amphoteric oxide which dissolves in alkalies and acids.

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$$
$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$$

3. When alumina is heated above 800°C in presence of C and N_2 then AlN is obtained.

$$Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO$$

Uses :

1. Alumina is used in the manufacture of a number of precious gems.
2. In the furnace lining and fire-bricks.
3. In the extraction of aluminium.
4. Fused bauxite called as corundum is used as abrassive.
5. In the manufacture of bauxite cement which quickly sets.

2. Aluminium hydroxide, $Al(OH)_3$:

Preparation :

(i) It is obtained as a gelatinous precipitate when hydroxides ions (e.g. sodium or potassium or ammonium hydroxides) or a solution of a carbonate, are added to a solution of an aluminium salt.

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3$$

e.g. $$Al_2(SO_4)_3 + 6NH_4OH \rightarrow 2Al(OH)_3\downarrow + 3(NH_4)_2SO_4$$

(ii) By the hydrolysis of aluminium chloride in presence of excess of water and at high temperature.

$$AlCl_3 + 3H_2O \rightarrow Al(OH)_3\downarrow + 3HCl$$

(iii) By bubbling CO_2 gas in sodium aluminate solution.

$$2NaAlO_2 + 3H_2O + CO_2 \rightarrow 2Al(OH)_3\downarrow + Na_2CO_3$$

Properties : (a) *Action of acids* : Aluminium hydroxide is amphoteric. When freshly prepared, it dissolves in acids to give salts.

$$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$$

(b) *Action of alkali* : It dissolves in alkalis to form aluminates.

$$Al(OH)_3+NaOH \rightarrow NaAlO_2+2H_2O$$

(c) *Action of heat* : When ignited at high temperatures, it is converted to its oxide.

$$2Al(OH)_3 \xrightarrow{\text{heat}} Al_2O_3+3H_2O$$

Uses : (i) Freshly prepared $Al(OH)_3$ absorbs colouring matter forming insoluble lakes. (ii) In the name of Aluminium Gel, it is used as drying agent.

3. **Aluminium chloride, $AlCl_3.6H_2O$:**

Preparation : It is prepared by dissolving Al, Al_2O_3 or $Al(OH)_3$ in dil. HCl.

$$2Al+6HCl \rightarrow 2AlCl_3+3H_2$$
$$2Al_2+6HCl \rightarrow 3AlCl_3+3H_2O$$
$$Al(OH)_3+3HCi \rightarrow AlCl_3+3H_2O$$

The solution of $AlCl_3$ so obtained is filtered and the filtrate is crystallised when colourless crystals of $AlCl_3.6H_2O$ are formed.

Properties : It is a colourless crystalline solid, soluble in water. It is a covalent compound. Anhydrous $AlCl_3$ is white deliquescent solid.

Anhydrous $AlCl_3$ or Ai_2Cl_6 :

Preparation : (i) Anhydrous aluminium chloride can be prepared by passing dry hydrogen chloride or dry chlorine over heated aluminium.

$$2Al+3Cl_2 \rightarrow 2AlCl_3 \rightarrow Al_2Cl_6$$
$$2Al+6HCl \rightarrow 3H_2+2AlCl_3 \rightarrow Al_2Cl_6$$

Since it is readily attacked by the moisture in the air, it must be prepared under anhydrous conditions. Soda lime absorbs moisture as well as excess of chlorine.

The reaction with chlorine is strongly exothermic.

$$\tfrac{1}{3}Al+\tfrac{1}{2}Cl_2 \rightarrow \tfrac{1}{3}AlCl_3;\ \Delta H=-209 \text{ kJ}$$

(ii) By heating a mixture of $Al_2O_3+6HCl+9H_2O$.

Note : The hydrated aluminium chloride, $AlCl_3.6H_2O$, does not yield anhydrous salt on heating due to the following reactions.

$$2AlCl_3.6H_2O \text{ or } 2[Al(H_2O)_6]Cl_3 \xrightarrow{\text{heat}} Al_2O_3+6HCl+9H_2O$$

Properties : *Physical* : (i) It is a white solid.

(ii) It sublimes at a temperature of about 180°C.

Chemical : (i) *Action of heat* : It sublimes at 180°C.

(ii) *Action of moisture* : When exposed to air, anhydrous $AlCl_3$ produces white fumes.

$$AlCl_3+3H_2O \rightarrow Al(OH)_3\downarrow+3HCl$$

(iii) *Action of NH_3* : Anhydrous $AlCl_3$ absorbs NH_3 because $AlCl_3$ is a Lewis acid or electron difficient compound.

$$AlCl_3+6NH_3 \rightarrow AlCl_3.6NH_3$$

(iv) *Action of alkalies* ($NaOH, KOH$) **solution** : When $NaOH$ or KOH solution is added dropwise to an aqueous $AlCl_3$ solution, a gelatinous precipitate of $Al(OH)_3$ is first formed which dissolves in excess of $NaOH$ solution to give a colourless solution of sodium aluminate.

$$AlCl_3+3NaOH \rightarrow Al(OH)_3+3NaCl$$
$$Al(OH)_3+NaOH \rightarrow NaAlO_2+2H_2O$$

(v) *Hydrolysis with water* : When $AlCl_3$ is dissolved in water it undergoes hydrolysis rapidly to produce $Al(OH)_3$ which is a weak base and HCl is a strong acid.

$$AlCl_3+3H_2O \rightarrow Al(OH)_3+3HCl$$

Hence, a solution of $AlCl_3$ in water is aeidic to litmus.

Uses : (i) $AlCl_3$ is used as a catalyst in Friedel-Craft's reaction.

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Ethyl chloride}}{C_2H_5Cl} \xrightarrow{AlCl_3} \underset{\text{Ethyl benzene}}{C_6H_5.C_2H_5} + HCl$$

(ii) It is used as a catalyst for cracking of petroleum.

4. Aluminium Sulphate, $Al_2(SO_4)_3.18H_2O$:

Preparation : It is prepared by dissolving aluminium hydroxide in concentrated sulphuric acid; the crystals $Al_2(SO_4)_3.18H_2O$ are obtained.

$$2Al(OH)_3+3H_2SO_4 \longrightarrow Al_2(SO_4)_3+6H_2O$$

(ii) By dissolving Al, freshly prepared $Al(OH)_3$ or Al_2O_3 in dilute H_2SO_4.

$$2Al+3H_2SO_4 \longrightarrow Al_2(SO_4)_3+3H_2$$
$$Al_2O_3+3H_2SO_4 \longrightarrow Al_2(SO_4)_3+6H_2O$$

The solution of $Al_2(SO_4)_3$ is filtered and crystallised to get $Al_2(SO_4)_3.18H_2O$.

Properties : It is white crystalline solid, soluble in water.

(i) *Action of heat* : It decomposes to give Al_2O_3.

$$Al_2(SO_4)_2.18H_2O \xrightarrow[\text{heat}]{340°C} Al_2(SO_4)_3+18H_2O$$

$$Al_2(SO_4)_3.18H_2O \xrightarrow{\text{ignite}} Al_2O_3+3SO_2+18H_2O$$

(ii) *Action of NaOH solution* : When a solution of $Al_2(SO_4)_3.18H_2O$ in water is treated with $NaOH$ solution, a white gelatinous precipitate of $Al(OH)_3$ is formed which dissolves in excess of $NaOH$ solution to give a colourless solution of sodium aluminate ($NaAlO_2$).

$$Al_2(SO_4)_3+6NaOH \longrightarrow 2Al(OH)_3+3Na_2SO_4$$
$$Al(OH)_3+NaOH \longrightarrow NaAlO_2+2H_2O$$

(iii) *Hydrolysis with water* : It hydrolyses with water to produce $Al(OH)_3$ and H_2SO_4.

$$Al_2(SO_4)_3+6H_2O \longrightarrow \underset{\text{weak base}}{2Al(OH)_3} + \underset{\text{strong acid}}{3H_2SO_4}$$

Hence the solution is acidic.

Uses : It is used

(i) in paper and tanning industry.

(ii) in making water proof clothes and papers.

(iii) for making potash alum.

(iv) as a mordant in dyeing industry and for making foam fire extinguishers.

5. Alums :

Alums are double salts having the formula, $M^+Al^{3+}(SO_4)_2^{-2}.12H_2O$. ($M^+=NH_4^+$, Na^+, k^+ etc) e.g.

$KAl(SO_4)_2.12H_2O$—Potash alum

$NH_4\,Al(SO_4)_2.12H_2O$—Ammonium alum.

Ordinary potash alum may be **prepared** :

(a) by allowing a solution containing equimolar proportions of potassium sulphate and aluminium sulphate.

(b) by warming aluminium foil in caustic potash solution to known strength until no more will dissolve.

$$2Al+2KOH+6H_2O \longrightarrow \underset{\text{Potassium aluminate}}{2KAl(OH)_4} + 3H_2$$

The clear solution is decanted and an amount of sulphuric acid, equivalent to four times the amount of caustic potash used to dissolve the aluminium, is added.

$$KAl(OH)_4+2H_2SO_4 \longrightarrow KAl(SO_4)_2+4H_2O$$

On crystallising, potash alum, $KAl\,(SO_4)_2.12H_2O$ separates. The solid contains $K(H_2O)_6$, $Al(H_2O)_6$ and SO_4^{2-} ions and is a double salt, since it gives the characteristic reactions of its constituent ions in solution.

It is possible to replace Al^{3+} ion by trivalent transition cations of about the same ionic size e.g. Cr^{3+}, Mn^{3+}, Fe^{3+} and Co^{3+} e.g.

$KCr\,(SO_4)_2.12H_2O$—Chrome (III) alum,

$NH_4Fe(SO_4)_2.12H_2O$—Ammonium iron alum.

(c) All alums can be prepared by allowing a solution containing equimolar proportions of the two sulphates to crystallise. In calculating their proportions, any water of crystallisation in the sample salt must be taken into consideration.

The alums separate from solution in octahedral crystals. They are isomorphous. Potash alum, like aluminium sulphate, is used as a mordant in dyeing since it forms aluminium hydroxide by hydrolysis. Other uses of alums are same as aluminium sulphate.

QUESTIONS

Long Type Questions :

1. How does Al occur in nature ? How is it extracted in pure form from bauxite ? [BIEC 1983]. How would you obtain—
   (a) Anhydrous $AlCl_3$ (b) Alumina (Al_2O_3)
   (c) Potash alum from Al ? [M. U. 1966 A; B. U. '67 A]
2. Describe the extraction of pure aluminium from bauxite ore containing low concentration of Fe_2O_3 in it. Describe the properties and uses of aluminium and its alloys. How does Al react with (a) HCl, (b) H_2SO_4, (c) HNO_3 [P. U. 1967 A; M. U. '69 A], (d) Fe_2O_3, (e) Chlorine, (f) Carbon ? [BIEC 1983]
3. Complete and balance the following reactions :
   (a) $Al_4C_3+H_2O \longrightarrow$ ——— + ——— [IIT 1968]
   (b) $Al+NaOH+H_2O \longrightarrow$ ——— + ——— [IIT 1969]
   (c) $AlN+H_2O \longrightarrow$ ——— + ———
   (d) $Al_2O_3+C+N_2 \longrightarrow$ ——— + ———
   (e) $AlCl_3+NaOH \longrightarrow NaAlO_2+$ ———
   (f) $Al_2O_3+C+Cl_2 \longrightarrow AlCl_3+$ ———
4. What happens when—
   (a) aluminium metal is boiled with caustic potash solution ? [P. U. 1976 A]
   (b) Al_2O_3 is heated with coke and Cl_2 is passed over it ? [IIT 1967 A]
   (c) Al_2O_3 is heated with coke and N_2 is passed over it ?
   (d) AlN is boiled with H_2O ?
   (e) $NaOH$ reacts with $AlCl_3$?

Short Type Questions :

5. How will you convert—
   (a) Al to Anhydrous $AlCl_3$?
   (b) Al_2O_3 to $AlCl_3$?
   (c) Al to pure Al_2O_3 and vice-versa ?
6. Write shortes on—
   (a) Alum [M. U. 1985] (b) Anhydrous $AlCl_3$ (c) Alumino thermite process.
7. How would you obtain pure Al from bauxite ? Give only reactions. [IIT 1969]
8. **Fill up the blank—**
   (a) Alumina is a ———. (b) Bauxite is ———. (c) Alum contains total number of ions ———. (d) Al is an ——— metal. (e) Duralumin is an ——— of ——— and———.
9. Explain the following—
   (a) A solution of aluminium sulphate in water is acidic.
   (b) The white ppt. obtained by addition of $NaOH$ solution, containing Al^{3+} ions, dissolves in excess of $NaOH$.
   (c) Aluminium containers are used for storing nitric acid.
   (d) $AlCl_3$ acts as Lewis acid.

10. Give formula of the following—
(a) Alumina (b) Bauxite (c) Potash alum (d) Cryolite (e) Aluminium carbide.

11. Name two important alloys of aluminium. Mention their uses.

12. How and under what conditions, does aluminium react with (a) caustic soda (b) chlorine (c) sulphuric acid ?

13. Write equations for the action of water on (i) aluminium carbide, (ii) aluminium nitride, (iii) aluminium phosphide.

14. Arrange the following in order of their increasing power of undergoing hydrolysis—$AlCl_3$, $NaCl$, $SnCl_2$. (Ans. $NaCl$, $SnCl_2$, $AlCl_3$)

Select and Write correct answer from the following—

15. Aluminium has the electronic configuration
(1) $Ne\ 3s^2 3p^1$ (2) $Ne\ 3s^2 3p^3$
(3) $Ar\ 4s^2 4p^1$ (4) $Ar\ 4s^2 4p^3$.

16. Al^{3+} contains
(1) 10 electrons, 10 protons (2) 10 electrons, 13 protons (3) 13 electrons and 13 protons (4) 16 electrons and 13 protons.

17. Bauxite is—
(1) Al_2O_3 (2) $Al_2O_3.H_2O$ (3) $Al_2O_3.2H_2O$ (4) Na_3AlF_6.

18. Potash alum is a—
(1) double salt (2) complex salt (3) simple salt (4) basic salt.

19. Mica is (1) an oxide (2) a sulphate (3) a halide (4) an alumino-silicate.

20. $Al(OH)_3$ is soluble in—
(1) $NaOH$ (2) HCl (3) all the above (4) none of these.

□□□

CHAPTER 18

TIN AND LEAD

18.1. Tin

Symbol : *Sn*. *At. No.* 50. *At. wt.* 118·70.
Electronic configuration : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^2$.

Occurrence :

The chief and important ore of tin are—

(i) *Cassiterite or Tinstone*, SnO_2 : It is associated with impurities of sand and earthly matter, Tungstates of iron and manganese ($FeWO_4$) and ($MnWO_4$) etc. It is mainly found in Malasia, Australia, China, Burma and in relatively smaller amounts in Hazaribagh (Bihar) and Orissa. India depends upon Malasia for her large supplies of tin.

(ii) *Tin pyrities* or *bell metal* are SnS_2, Cu_2S, Fe_2S_2 or (Cu_2FeSnS_4).

Extraction :

It is maintly obtained from Tinstone (SnO_2) and involves the following steps :

(i) *Concentration* : The powdered ore which contains 5 – 10% of SnO_2 is first made free from the impurities by

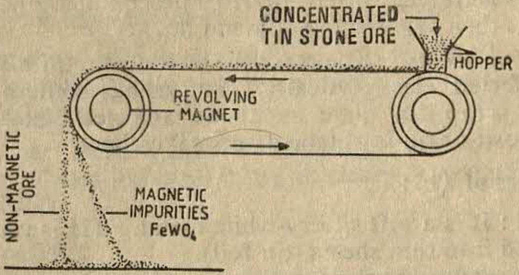
(a) *Gravity method* : The powdered ore is washed in a current of water when the lighter sand and earthly matter flows away while the heavier ore particles are left at the bottom.

(b) *Electromagnetic method* : The magnetic impurities of wolframite ($FeWO_4$) are removed by this method. The washed ore is dropped on a belt moving on electro-magnetic rollers. The wolframite particles being attracted by the magnet fall in separate heap and near the magnet.

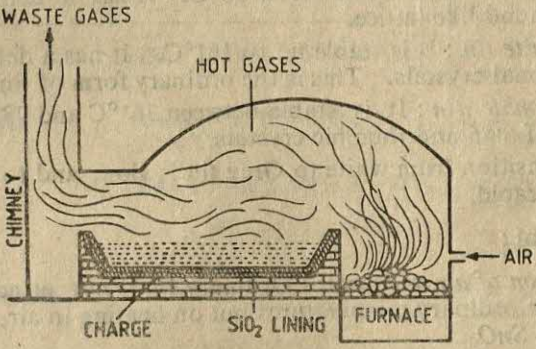
(c) *Roasting* : The ore is then roasted in a current of air whereby the arsenic and sulphur are removed as As_2O_3 and SO_2 which volatilize off. The iron and copper pyrities are converted into oxides and sulphates.

(d) *Acid leachings* : The roasted ore is treated will dil. H_2SO_4 to dissolve out the oxides of *Cu*, *Fe* and *Zn* and to convert sulphides into soluble sulphates. Tin dioxide, SnO_2, remains unattached.

(ii) *Smelting* : The concentrated ore is now mixed with anthracite coal and lime stone (flux) and heated at about 1200°C – 1300°C in a reverberatory furnace. The oxide is reduced to metal which having a very low m. p. (232°C) collects at the base in the molten state and is drawn off from time to time.



Electromagnetic Method



Reverberatory Furnace for Smelting Tin

(iii) *Refining* : The crude metal so obtained contains impurities of copper, iron, tungsten etc. and is refined by treating it successively as below :

(a) *Liquation* : The crude tin is heated on the sloping hearth of a reverberatory furnace when the easily fusible tin melts (m.p. 232°C) and flows away, leaving behind the impurities of copper, iron tungsten etc.

(b) *Poling* : The molten metal is stirred by poles of green wood whereby any tin oxide left unreduced gets reduced by the hydrocarbons of the wood, tin so obtained is 98% pure.

(c) *Electrolysis* : Cathode—Pure Tin sheet. Anode—Impure Tin sheet. Electrolyte—$SnSO_4$ containing H_2SiF_4 and H_2SO_4.

On passing the current, tin dissolves from anode and is deposited at cathode in very pure (98·8%) condition.

Recovery of Tin from Tin plate scraps :

(i) *First Method* : The tin scraps are first washed with dilute alkali to remove grease, then with water and dried. These are packed in big iron cylinders and treated with Cl_2. Tin combines with Cl_2 to form stannic chloride ($SnCl_4$) which is liquid under these conditions. This is treated with NH_4OH to precipitate stannic hydroxide. The latter is then smelted to get metal tin.

(ii) *Second Method* : The recovery of tin from tin plate scrap can also be affected electrolytically. But using sodium cyanide an electrolyte, scrap tin plate as anode and steel plate as cathode, a spongy deposit of tin is obtained on steel cathode.

Properties of Tin :

Physical : It is a soft silvery-white metal. Tin is very ductile and can be rolled into thin sheets (tin foil).

Allotropy of Tin : Tin exists in three forms :

(a) *Grey tin* : It is stable below 18°C. It has a density of 5·75 and a diamond like lattice.

(b) *White tin* : It is stable up to 161°C. It has a density of 7·28 and tetragonal crystals. This is the ordinary form of tin.

(c) *Rhombic tin* : It is stable between 161°C and 232°C. It has a density of 6·56 and rhombic crystals.

The transition from white to Grey tin is slow; and to rhombic tin (brittle) is rapid.

Chemical :

(i) *Action of air and water* : Ordinary tin is not attacked by air or water at ordinary temperatures but on heating in air, it forms tin (IV) oxide, SnO_2.

(ii) *Action of acids* : Dilute acids attack it only slowly, but it dissolves readily in concentrated hydrochloric acid to give stannous chloride.

$$Sn + 2HCl \rightarrow SnCl_2 + H_2\uparrow$$

Concentrated nitric acid reacts with tin to form hydrated tin (IV) oxide and some tin (II) nitrate, $Sn(NO_3)_2$:

$$Sn + 4HNO_3 \rightarrow SnO_2 + 4NO_2 + 2H_2O$$

(iii) *Action of halogens* : It is readily attacked by the halogens to give the corresponding tetrahalide.

$$Sn + 2Cl_2 \rightarrow SnCl_4$$

(iv) *Action of alkali* : It dissolves in hot concentrated alkali to form hexahydroxo-stannate (IV) :

$$Sn + 4H_2O + 2OH^- \rightarrow [Sn(OH)_6]^{2-} + 2H_2\uparrow$$
$$Sn + 2NaOH + 4H_2O \rightarrow Na_2[Sn(OH)_6] + 2H_2\uparrow$$

(v) *Action of sodium* : Finely divided tin is also dissolved by a solution of sodium in liquid ammonia, forming the red compound Na_4Sn_9. This compound is ionic containing polyanion Sn_9^{4-}.

Uses of tin : Tin is used in (a) tin plating and (b) food containers.

Tin plating :

It is a process in which iron sheets are plated with tin. Tin plating may be done by the following methods :

(i) Thin sheets of iron or mild steel, previously cleaned by immersion in dilute acid (*picling*) are dipped in molten tin, which forms a thin surface layer.

(ii) Another method involves electrolytic deposition of tin on the article to be placed (*cathode*) using an electrolyte of acidified tin (II) sulphate, $SnSO_4$.

Alloys of Tin :

Name of alloys	*Composition*	*Uses*
1. Bronze	$Cu=75-90\%$; $Sn=10-25\%$	In making utensils, statues, coins.
2. Gun metal	$Cu=87\%$; Tin$=10\%$; $Zn=3\%$	In making guns, glass, castings.
3. Solder	$Sn=50-50\%$; $Pb=50-43\%$	In soldering damaged and broken articles.
4. Pewter	$Sn=75\%$; $Pb=25\%$	In making utensils.
5. Babbit Metal	$Sn=90\%$; $Sb=7\%$; $Cu=3\%$	For making bearings of machinery.
6. Britannia Metal	$Sn=93\%$; $Pb=5\%$; $Cu=2\%$	In making spoons, forks etc.

18.2. Compounds of Tin

Tin forms two series of salts (i) stannous and (ii) stannic in which the metal shows oxidation state +2 and +4 respectively. Stannous salts are good reducing agents as they are readily oxidised to stannic salts.

1. Stannous oxide, *SnO* :

Preparation : It is formed by heating stannous hydroxide or oxalate.

$$Sn(OH)_2 \rightarrow SnO + H_2O$$
$$(COO)_2\,Sn \rightarrow SnO + CO + CO_2$$

It is also obtained when caustic soda solution is added to stannous chloride solution.

$$SnCl_2 + 2NaOH \rightarrow Sn(OH)_2 + 2NaCl$$
$$Sn(OH)_2 \rightarrow SnO + H_2O$$

Properties :

(i) It is a dark-grey powder which forms stannic oxide on heating in air.

$$2SnO+O_2\rightarrow 2SnO_2$$

(ii) It is an amphoteric oxide which reacts both with acids and alkalies forming salts.

$$SnO+2HCl\rightarrow SnCl_2+H_2O$$

$$SnO+2NaOH\rightarrow \underset{\text{Sod. Stannite}}{Na_2SnO_2}+H_2O$$

The stannites are known only in aqueous solutions which are oxidised to stannates by absorbing oxygen from air.

$$2Na_2SnO_2+O_2\rightarrow 2Na_2SnO_3$$

2. Stannic Oxide, SnO_2 :

Preparation :

It is obtained by calcining metastannic acid which is obtained by heating tin in nitric acid.

$$Sn+4HNO_3\rightarrow H_2SnO_3+4NO_2+H_2O$$

$$H_2SnO_3\rightarrow SnO_2+H_2O$$

Properties :

(i) It is a white powder. It turns yellow on heating and then brown and regains its original colour on cooling.

(ii) It is not acted upon by acids other than sulphuric acid, which forms stannic sulphate but on dilution stannic oxide is precipitated.

$$SnO_2+2H_2SO_4\rightarrow Sn(SO_4)_2+2H_2O$$

$$Sn(SO_4)_2+2H_2O\rightarrow SnO_2+2H_2SO_4$$

(iii) It is readily soluble in alkalies forming stannates.

$$SnO_2+2KOH\rightarrow K_2SnO_3+H_2O$$

Uses : (i) In the manufacture of milky glass.

(ii) In making electric light shades.

3. Stannous Chloride, $SnCl_2.2H_2O$:

Preparation :

(i) It is obtained in *hydrated* form by dissolving tin in conc. HCl and concentrating the solution to crystallisation.

$$Sn+2HCl\rightarrow SnCl_2+H_2$$

(ii) *Anhydrous* salt is obtained by passing dry HCl gas over heated tin.

$$Sn+2HCl\ (g)\rightarrow SnCl_2+H_2$$

Properties :

(i) It is colourless crystalline solid, and soluble in water. It is hydrolysed by excess of water forming hydroxy chloride.

$$SnCl_2+H_2O \rightarrow Sn(OH)Cl+HCl$$

(ii) *As reducing agent* : It acts as a reducing agent because it looses electron during a chemical reaction.

$$Sn^{+2} \rightarrow Sn^{+4}+2e$$

(ous) (ic)

It reduces mercuric to mercurous state, ferric to ferrous state, cupric to cuprous state and auric chloride to aurous chloride.

(a) *Reaction with $HgCl_2$* :

$$HgCl_2+SnCl_2 \rightarrow Hg+SnCl_4$$

$$(Hg^{++}+Sn^{++} \rightarrow Hg+Sn^{+4})$$

In this reaction mercuric chloride is reduced to metallic mercury.

$$2HgCl_2+SnCl_2 \rightarrow Hg_2Cl_2+SnCl_4$$

$$(2Hg^{++}+Sn^{++} \rightarrow Hg_2^{++}+Sn^{+4})$$

In this case mercuric chloride is reduced to mercurous chloride.

(b) *Reaction with Ferric chloride ($FeCl_3$)*:

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$$

Ferric chloride Ferrous chloride

$$(2Fe^{+3}+Sn^{+2} \rightarrow 2Fe^{+2}+Sn^{+4})$$

(c) *Reaction with cupric chloride ($CuCl_2$)* :

$$2CuCl_2+SnCl_2 \rightarrow SnCl_4+Cu_2Cl_2$$

Cupric chloride Cuprous chloride

$$(2Cu^{++}+Sn^{++} \rightarrow Sn^{+4}+Cu_2^{++})$$

(d) *Reaction with Auric chloride ($AuCl_3$)* :

$$2AuCl_3+3SnCl_2 \rightarrow 3SnCl_4+2Au$$

Auric chloride Gold

$$(2Au^{+++}+3Sn^{++} \rightarrow 3Sn^{+4}+2Au)$$

(iii) *Action of H_2S* : It gives brown precipitate of stannous sulphide (SnS) with H_2S.

$$SnCl_2+H_2S \rightarrow SnS+2HCl$$

(iv) *Action of MOH ($M=Na, K$)* : When sodium hydroxide solution is added to $SnCl_2$ solution then stannous hydroxide is first formed which dissolves in excess of alkali giving sodium stannite.

$$SnCl_2+2NaOH \rightarrow Sn(OH)_2+2NaCl$$

(Little $NaOH$)

$$SnCl_2+4NaOH \rightarrow Na_2SnO_2 + 2H_2O$$

Sod. Stannite (Excess of $NaOH$)

Uses : (i) As a mordant in dyeing.

(ii) As a reducing agent and laboratory reagent.

(iii) In the extraction of gold.

(iv) In the preparation of "Purple of cassius" used as colouring matter.

4. Stannic chloride, $SnCl_4$:

Preparation :

It is prepared by passing chlorine over tin heated in a retort.

$$Sn + 2Cl_2 \rightarrow \underset{\text{Stannic chloride}}{SnCl_4}$$

Stannic chloride distills over as a colourless liquid and is collected in a receiver protected from moisture by $CaCl_2$ tube.

Properties :

(i) It is colourless and unpleasant smelling fuming liquid, b.p. 114°C.

(ii) It absorbs moisture from air forming soluble crystalline hydrates.

$$SnCl_4.3H_2O;\ \underset{\text{(Butter of tin)}}{SnCl_4.\ 5H_2O};\ SnCl_4.6H_2O;\ SnCl_4.8H_2O$$

It is hydrolysed by water to form colloidal solution of stannic acid.

$$SnCl_4 + 4H_2O \rightarrow Sn(OH)_4 + 4HCl$$

(iii) It forms double salts with NH_3, $NOCl$, N_2O_4 etc.

$$(NH_4)_2.SnCl_6;\ SnCl_4.NOCl$$

(iv) It reacts with HCl to form hexachloro stannic acid, H_2SnCl_6.

$$SnCl_4 + 2HCl \rightarrow H_2SnCl_6$$

Uses : Its pentahydrate, named *butter of tin*, and amm. chlorostannate, named *pinc salt*, are used as mordants in dyeing.

18.3 Lead

Symbol : *Pb*. *At. No.* 82 *At. wt.* 207·2

Electronic configuration : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^2$.

Occurrence : It is found in abundance in nature. It occurs in combined state.

Galena, Lead sulphide	Pbs
Cerrusite, Lead carbonate	$PbCO_3$
Anglesite, Lead sulphate	$PbSO_4$
Matlokite	$PbCl_2.PbO$.

Extractions :

The chief and important ore from which the metal lead is obtained is *Galena PbS* which contains 5-10% *Pb*. It is generally associated with sulphides of *Ag*, *Zn*, *Sb* and silicon impurities. The extraction of the metal involves the following steps :

(i) *Concentration* : The ore is powdered, sieved and then concentrated by *froth floatation process*.

(ii) *Reduction* : There are two methods employed for reduction which depend upon the lead content of the ore.

(a) *Air Reduction Process* (For ores rich in lead) :

The concentrated ore is roasted on the hearth of reverberatory furnace (see extraction of Tin) at a moderate temperature (below 75°A) and in limited supply of air. A part of lead sulphide is oxidised to oxide and part to sulphate.

$$2PbS+4O_2\rightarrow 2PbO+2SO_2$$
$$PbS+2O_2\rightarrow PbSO_4$$

The air supply is now cut off by closing the doors *D*, *D* and temperature of the furnace is raised. *PbO* and $PbSO_4$ are reduced by unchanged *PbS* into metal lead which is drawn off from the bottom of the furnance.

$$PbS+2PbO\rightarrow 3Pb+SO_2$$
$$PbS+PbSO_4\rightarrow 2Pb+2SO_2$$

The method has *now been largely suspended.*

(b) *Carbon Reduction Process* (For ores even poor in lead) The cocentrated ore is mixed with lime (flux) and roasted in blast of air in a sinterer. The sulphur present in the ore burns and lead sulphide is mainly converted into oxide.

The sintered ore is then mixed with coke and lime and smelted in a small blast furnace., It is 15-20 ft. high and 4-5 ft. in diameter. It is made of steel plates lined with fire bricks and is water-jacketted. The coke reduces lead oxide into lead.

$$PbO+C\rightarrow Pb+CO$$
$$PbO+CO\rightarrow Pb+CO_2$$

The lime combines with silica present in it to form slag of calcium silicate. Moreover, being more basic than *PbO* prevents the loss of lead as lead silicate.

$$CaO+SiO_2\rightarrow CaSiO_3$$
$$PbSiO_3+CaO\rightarrow CaSiO_3+PbO$$

The molten lead covered with a layer of slag collects at the bottom and is drawn off through the tap hole.

(iii) *Refining* : The metal lead obtained by any of the methods contains *Cu*, *Ag*, *Bi*, *As*, *Sb*, *Sn* and *Fe* as impurities. These are removed as below—

(a) *Liquation* : The impure metal is melted on shallow hearth of a reverberatory furnace and a current of air is passed over it. The base metals *Cu*, *Sn* and *Fe* are oxidised and come to the surface in the form of a scum which is removed.

(b) *Desilverisation* : *Ag* is removed by Parkes and Pattinson's process.

(c) *Electrolytic Refining* : It is further refined by Bett's electrolytic process which consists of :

Anode	..	Impure lead
Cathode	..	Pure lead
Electrolyte	..	Soln. of lead silico fluoride, $PbSiF_6$, containing 8-12% of H_2SiF_4

On passing electric current, pure lead is deposited on cathode while less electropositive impurities *Ag*, *Au*, *Sb*, *Cu* fall down below anode as anode mud, and more electropositive *Fe*, *Ni*, *Zn* remain in the solution.

Properties of Lead :

Physical : (a) It is a bluish grey metal and possesses, when freshly cut, a bright metallic lustre which, however, becomes dull on exposure to air due to the formation of a thin layer of the oxide on the surface.

(b) It is so soft that it can be cut with a knife.

(c) It marks paper.

(d) It is malleable but not very ductile.

(e) Its specific gravity is 11·34. It melts at 327·4°C and boils at 172°C.

Chemical :

1. *Action of air* : It is not attacked by dry air but gets tarnished in moist air due to the formation of a thin film of the basic carbonate which prevents it from further action.

2. *Action of air and heat* : When lead is heated in air or oxygen, it is oxidised to litharge (PbO) and red lead (Pb_3O_4).

$$2Pb+O_2\rightarrow 2PbO$$
$$6PbO+O_2\rightarrow 2Pb_3O_4$$

3. *Action of water* : Lead is not attacked by pure air-free water (except at the boiling point). It slowly decomposes steam at high temperatures. It is readily corroded by water containing dissolved air forming lead hydroxide which is appreciably soluble in water. The solvent action of water, known as "*Plumbo Solvency*" is greater when water contains nitrates, organic acids and ammonium salts. The reaction is, however, retarded by certain salts such as phosphates, carbonates and sulphates since they form a coating of insoluble lead salts on the surface of the metal which protects it from further action. Thus, hard water has no solvent action on lead.

4. *Action of acids* : It does not react with dil. HCl or H_2SO_4. When lead is boiled with conc. HCl, hydrogen gas is evolved and a solution of H_2PbCl_4 is formed.

$$Pb+2HCl\rightarrow PbCl_2+H_2\uparrow$$
$$PbCl_2+2HCl\rightarrow H_2PbCl_4$$

When lead is heated with conc. H_2SO_4, sulphur dioxide gas is evolved but the reaction soon stops due to the formation of an insoluble layer of $PbSO_4$ over lead.

$$Pb+2H_2SO_4 \rightarrow PbSO_4+2H_2O+SO_2\uparrow$$

Lead reacts with dilute HNO_3 and liberates nitric oxide gas.

$$3Pb+8HNO_3 \rightarrow 3Pb(NO_3)_2+2NO+4H_2O$$

Lead reacts with hot conc. HNO_3 more vigorously liberating fumes of NO_2.

$$Pb+4HNO_3 \rightarrow Pb(NO_3)_2+2NO_2+2H_2O$$

5. *Action of alkalies* : Lead is slowly attacked by caustic alkalies with the formation of soluble plumbite.

$$Pb+2NaOH \rightarrow Na_2PbO_2+H_2$$

6. *Reaction with non-metals* : Lead reacts with chlorine and sulphur to give chlorides and sulphides.

$$Pb+Cl_2 \rightarrow PbCl_2$$
$$Pb+S \rightarrow PbS$$

7. *Formation of Lead tree* : When a rod of zinc or Fe is dipped in a solution of lead acetate, a crystalline growth of lead tree is slowly formed.

$$Pb(CH_3COO)_2+Zn \rightarrow Zn(CH_3COO)_2+Pb$$

Uses : Lead is a very useful metal. It is used for making

(a) alloys;

(b) lead accumulators, lead shots, and covering of electric cables;

(c) lead pipes;

(d) lead chambers for the manufacture of H_2SO_4;

(e) $Pb-As$ alloy bullets.

18.4 Compounds of Lead

1. Lead (II) Oxide, Lead monoxide, Litharge, Massicot, *PbO* :

Preparation :

(i) It is obtained when molten lead is oxidised by a blast of air.

$$\underset{\text{(molten)}}{2Pb} + \underset{\text{(air)}}{O_2} \rightarrow 2PbO$$

(ii) Massicot is obtained by heating lead carbonate or lead nitrate.

$$PbCO_3 \rightarrow PbO+CO_2$$

Properties :

(i) It is the stable form at room temperature, but massicot changes only very slowly to litharge under ordinary conditions.

It is only slightly soluble in water.

(ii) It is easily reduced to the metal when heated with reducing agent such as H_2, C and CO.

$$PbO+H_2 \rightarrow Pb+H_2O$$
$$PbO+C \rightarrow Pb+CO$$
$$PbO+CO \rightarrow Pb+CO_2$$

(iii) It is an *amphoteric* oxide. It dissolves easily in acids to give lead (II) salts.

$$PbO+2HCl \rightarrow PbCl_2+H_2O$$

It dissolves slowly in alkalies to give hydroxoplumbites e.g. $Na_2Pb(OH)_4$.

$$PbO+2NaOH+H_2O \rightarrow Na_2[Pb(OH)_4]$$

Uses : It is used

(i) in the rubber industry;

(ii) in the manufacture of flint glasses, enamels and storage batteries.

2. **Red Lead, Pb_3O_4 (*Minium*) :**

Preparation :

It is prepared by heating litharge to 400°C in excess of air.

$$\underset{\text{Litharge}}{6PbO}+O_2 \rightarrow \underset{\text{Red lead}}{2Pb_3O_4}$$

Properties :

(i) It is red crystalline solid, and insoluble in water.

(ii) *Action of heat* : When heated above 450°C, it gives off oxygen.

$$2Pb_3O_4 \rightarrow 6PbO+O_2$$

(iii) *Action of acids* : (a) It reacts with conc. HCl to give chlorine.

$$\begin{array}{ll} Pb_3O_4 \rightarrow 3PbO+O & \\ PbO+2HCl \rightarrow PbCl_2+H_2O & (\times 3) \\ 2HCl+O \rightarrow H_2O+Cl_2 & \\ \hline Pb_3O_4+8HCl \rightarrow 3PbCl_2+4H_2O+Cl_2 & \end{array}$$

(b) It reacts with conc. H_2SO_4 to give oxygen.

$$\begin{array}{ll} Pb_3O_4 \rightarrow 3PbO+O & (\times 2) \\ PbO+H_2SO_4 \rightarrow PbSO_4+H_2O & \\ O+O \rightarrow O_2 & \\ \hline 2Pb_3O_4+6H_2SO_4 \rightarrow 6PbSO_4+6H_2O+O_2 & \end{array}$$

(c) It reacts with conc. HNO_3 to give $Pb(NO_3)_2$ and PbO_2.

$$\begin{array}{l} Pb_3O_4 \rightarrow 2PbO+PbO_2 \\ 2PbO+4HNO_3 \rightarrow 2Pb(NO_3)_2+2H_2O \\ \hline Pb_3O_4+4HNO_3 \rightarrow PbO_2+2Pb(NO_3)_2+2H_2O \end{array}$$

Uses :

(i) As a red pigment.

(ii) As oxidising agent in glass and match industry.

3. Lead dioxide, PbO_2 :

Preparation :

(i) It is prepared by heating lead acetate with sodium hypochlorite in presence of alkali.

$$\underset{\text{Lead acetate}}{(CH_3COO)_2Pb}+NaOCl+2NaOH\rightarrow PbO_2+NaCl+2CH_3COONa+H_2O$$

Lead dioxide is obtained as brown powder insoluble in water.

(ii) It is obtained by the action of HNO_3 on red lead.

$$Pb_3O_4+4HNO_3\rightarrow PbO_2+\underset{\text{solution}}{2Pb(NO_3)_2}+2H_2O$$

Properties :

(i) It is chocolate brown powder, insoluble in water.

(ii) *As oxidising character* : Since it evolves oxygen on heating hence it acts as an oxidising agent.

$$PbO_2\rightarrow PbO+O$$

(a) It oxidises conc. HCl to chlorine.

$$\begin{array}{c} PbO_2\rightarrow PbO+O \\ 2HCl+O\rightarrow H_2O+Cl_2 \\ PbO+2HCl\rightarrow PbCl_2+H_2O \\ \hline PbO_2+4HCl\rightarrow PbCl_2+2H_2O+Cl_2 \end{array}$$

(b) It oxidises manganous salt to permanganate.

$$2\overset{+2}{Mn}SO_4+5\overset{+4}{Pb}O_2+6HNO_3\rightarrow 2H\overset{+7}{Mn}O_4+2\overset{+2}{Pb}SO_4+3Pb(NO_3)_2+2H_2O$$

$\nearrow\downarrow\quad\nearrow\uparrow$

② $\times 5e^-=$ ⑤ $\times 2e^-$

(iii) *As amphoteric character* : It dissolves in alkalies to form plumbates and in acid to form salts.

$$PbO_2+2NaOH\rightarrow \underset{\text{Sod. plumbate}}{Na_2PbO_3}$$

$$2PbO_2+2H_2SO_4\rightarrow 2PbSO_4+2H_2O+O_2$$

$$PbO_2+4HCl\rightarrow PbCl_2+2H_2O+Cl_2$$

Uses : (i) In lead accumulator.

(ii) As oxidising agent in the laboratory.

(iii) In safety matches.

4. Sugar of Lead, $(CH_3COO)_2Pb.3H_2O$:

Preparation : It is prepared by dissolving lead oxide (PbO) or carbonate in hot dil. acetic acid, followed by concentration.

$$PbO+2CH_3COOH\rightarrow (CH_3COO)_2Pb+H_2O$$

$$PbCO_3+2CH_3COOH\rightarrow (CH_3COO)_2Pb+CO_2+H_2O$$

Properties :

(i) It is white crystalline solid, easily soluble in water.
(ii) Its taste in sweet but it is poisonous.

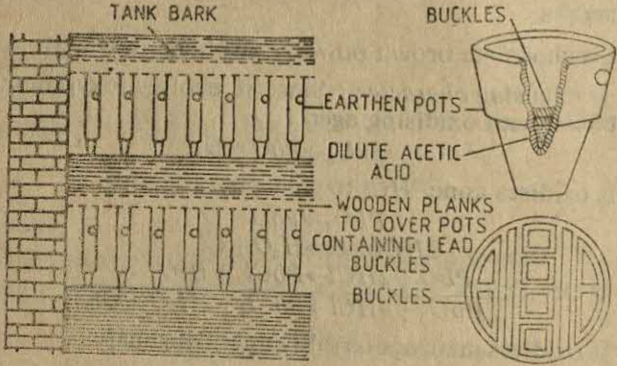
Uses :

(i) In dying and calico printing.
(ii) In manufacture of chrome yellow and other pigment.
(iii) In medicine as lead lotion.

5. **White Lead**, $2PbCO_3.Pb(OH)_2$, *(Basic Lead carbonate)* :

Manufacture : Two methods are used—

(i) *Dutch Process* : This is an old process, though it gives white lead of excellent quality. It is based on the action of acetic acid on metal lead in presence of moist air and CO_2.



A number of earthen wave pots having shelves and containing supported perforated lead discs called *Buckles*, are placed one above the other in rows and covered with alternate layers of spent horse dung in a shed. The pots are kept as such for 5 or 6 weaks :

During this interval fermentation takes place. CO_2 is evolved and heat produced volatilises acetic acid which reacts with lead to form white lead as below :

$$2Pb+2H_2O+O_2(\text{air})\rightarrow 2Pb(OH)_2$$

$$Pb(OH)_2+2CH_3COOH\rightarrow Pb(CH_3.COO)_2+2H_2O$$

$$Pb(OH)_2+Pb(CH_3COO)_2\rightarrow \underset{\text{Basic lead acetate}}{Pb(CH_3COO)_2.Pb(OH)_2}$$

$$2Pb(CH_3COO)_2.Pb(OH)_2+4CO_2+2H_2O \rightarrow 2\underset{\text{white lead}}{[2PbCO_3.Pb(OH)_2]}+4CH_3COOH$$

(ii) *Carter's process* : Molten lead is atomised with a jet superheated steam and introduced into rotating wooden cylinders. Dil. acetic acid is sprayed into it and a mixture of CO_2 and air is also admitted. The process takes place as before and is completed much earlier in about 15 days.

Uses :

It is used as white pigment.

6. Chrome yellow, $PbCrO_4$:

It is obtained as a yellow precipitate by mixing potassium chromate with lead acetate solution.

$$(CH_3COO)_2Pb+K_2CrO_4 \rightarrow PbCrO_4+2CH_8COOK$$

It is used as a yellow pigment. If less deep colour is required, it is mixed with white lead or lithopone.

7. Lead Tetra Ethyl, $Pb(C_2H_5)_4$:

Preparation : (i) By treating $PbCl_2$ with ethyl magnesium iodide.

$$2PbCl_2+4C_2H_5MgI \rightarrow Pb(C_2H_5)_4+4Mg$$

(ii) By heating ethyl chloride with *Na-Pb* alloy under pressure.

$$4C_2H_5Cl+4Na.Pb \rightarrow Pb(C_2H_5)_4+3Pb+4NaCl$$

Properties :

It is a liquid (b.p. 200°C). It is insoluble in water but soluble in ether when passed through hot tube (600° – 800°C) at low pressure (1-2 mm.) in an inert atmosphere, it is decomposed forming free ethyl radicals.

$$(C_2H_5)_4Pb \rightarrow 4C_2H_5+Pb$$

Uses. As TEL it is extensively used as an antikroch compound i.e. for raising the octarc number of petrol. 1-3 ml of **TEL** is mixed per gallon of petrol.

Typical Questions with Answers

1. How will you distinguish between stannous salts and stannic salts ?

Solution :

Reagents	*Stannous salts*	*Stannic Salts*
1. Action of mercuric chloride	A white ppt. of mercurous chloride is formed which turns grey due to the formation of metallic mercury. $SnCl_2+2HgCl_2 \rightarrow SnCl_4 + Hg_2Cl_2$ $SnCl_2+Hg_2Cl_2 \rightarrow 2Hg+SnCl_4$	No precipitate is obtained.
2. On adding zinc pieces to the salt solution	A spongy deposit of tin is formed on zinc pieces.	No action.

2. Explain the following—

(a) Damaged kerosene tins deteriorate quickly.

(b) Lead pipes are not safe for drinking water.

(c) Lead pipes are only slowly corroded by HCl or H_2SO_4 while they are more readily corroded by acetic acid and nitric acid.

Solution. (a) Kerosene tins are made of tin plated iron sheets. When damaged the layer of tin is removed from the surface so that the free surface of iron is exposed to air. It consequently gets rusted in course of time and is deteriorated much earlier than the undamaged tin.

(b) Water containing dissolved air can readily attack lead forming water soluble lead hydroxide. This solvent action of water is **known as Plumbo-solvency.**

$$2Pb+2H_2O+O_2 \rightarrow \underset{\text{Lead hydroxide}}{2Pb(OH)_2}$$

Due to poisonous nature of metal lead, the use of lead pipes for conveying drinking water is thus not desirable.

(c) Lead is very slightly attacked by dilute HCl or H_2SO_4 in the cold because a thin film of insoluble lead chloride or lead sulphate is formed over its surface which prevents further action. On the other hand lead pipes are readily dissolved by acetic acid and nitric acid due to the formation of soluble lead acetate and lead nitrate respectively.

$$2Pb+4CH_3COOH+\underset{\text{(air)}}{O_2} \rightarrow 2Pb(CH_3COO)_2+2H_2O$$

$$3Pb+8HNO_3 \rightarrow 3Pb(NO_3)_2+2NO+2H_2O.$$

Thus due to protective action of film of lead chloride and lead sulphate formed on the surface of lead pipes they are not corroded by dil. HCl or H_2SO_4 while due to solubility of lead pipes in acetic acid and HNO_3, they are readily corroded by them

Exercises

Long Type Questions :

1. What are the important ores of Tin ?
   How is it extracted from Cassiterite ore ? Give the basic principles involved. **(R. U. 1966 A; Bhag. U. '69 A)**
2. What happens when Tin reacts with
   (a) Cl_2 (b) HCl (c) H_2SO_4 (d) $NaOH$ (e) Sulphur ? **(Bhag. U. 1969 A)**
3. What happens when stannous chloride reacts with
   (a) $HgCl_2$ (b) $FeCl_3$ (c) H_2S (d) Cl_2 ? **(P. U. 1975)**

4. What are the ores of Lead? How is it extracted from Galena? What happens when lead reacts with
   (a) HCl (b) HNO_3 (c) $NaOH$ (d) Cl_2?
5. Write notes on (Give the preparation, properties and uses)
   (a) Stannous chloride (b) Plumbo-solvency (c) Chrome Yellow (d) TEL (e) White lead.

Short Type Questions :

6. Explain the following—
   (a) Sn^{+2} and Fe^{+3} cannot coexist in appreciable concentrations in the same solution. **(I.I.T. 1977, '80)**
   (**Hint**. $2Fe^{+3}+Sn^{+2}\rightarrow 2Fe^{+2}+Sn^{+4}$)
   (b) Red Lead is used in paints. **(I.I.T. 1977)**
   (c) Tin is used in making solder. **(I.I.T. 1977)**
   (**Hint**. Because it is easily fusible alloying metal.)
   (d) The lead of lid pencils is not Lead but graphite. **(I.I.T. 1970 A)**
7. State whether the following sattement is true or false?
   (i) Pb and Sn are amphoteric metals.
   (ii) PbO reacts with SO_3 to form $PbSO_4$.
   (iii) $SnCl_2$ is an oxidising agent.
   (iv) Red lead is PbO.
   (v) Litharge is PbO.
   (vi) Lead pencil contains graphite.
8. How would you obtain?
   (a) Red lead from litharge. **(I.I.T 1968 A)**
   (b) $SnCl_4$ from Sn. **(I.I.T. 1968 A)**
   (c) $SnCl_2$ from Sn. **(I.I.T. 1968 A)**
9. How will you distinguish between
   (a) $PbCl_2$ and $SnCl_2$ (b) $SnCl_2$ and $SnCl_4$ (c) $Pb(NO_3)_2$ and $PbCl_3$.
10. What happens when
    (i) $SnCl_2$ reacts with (a) $HgCl_2$ (b) $NaOH$ (c) $FeCl_3$ (d) H_2S (e) $AuCl_3$.
    (ii) Sn reacts with (a) HNO_3 (b) KOH.
    (iii) PbO_2 reacts with (a) $NaOH$ (b) HCl (c) $MnSO_4$ in presence of HNO_3.
11. How will you bring about the following conversions?
    (a) Sn to $SnCl_2$ and vice-versa.
    (b) $SnCl_2$ to $SnCl_4$ and vice-versa.
    (c) $Pb(NO_3)_2$ to $PbSO_4$ and vice-versa.
12. Fill up the blank :
    (a) Sn is extracted from.....................
    (b) Galena is an ore of..........................
    (c) $SnCl_2$ is a............agent.
    (d) $SnCl_4$ contains..............bond.
    (e) White lead is used in..............
    (f) TEL is used in petrol as...........substance.

13. Match *A* with *B* :

Formula of the compounds (*A*)	*Name of the compounds* (*B*)
(i) $SnCl_4.5H_2O$	(a) Litharge
(ii) $PbCrO_4$	(b) Red Lead
(iii) Pb_3O_4	(c) Sugar of lead
(iv) PbO	(d) Butter of tin.
(v) PbS	(e) White lead
(vi) $(CH_3COO)_2Pb.3H_2O$	(f) Chrome yellow
(vii) $2PbCO_3.Pb(OH)_2$	(g) TEL
(viii) $Pb(C_2H_5)_4$	(h) G

14. The colour of Pb_3O_4 is
(1) Yellow (2) Brown (3) Red (4) Blue (5) Green. (P.M.D.T. 1976)

15. White Lead is
(1) PbO (2) $2PbCO_3$ (3) $2PbCO_3.Pb(OH)_2$ (4) $Pb(OH)_2.Pb(CH_3COO)_2$. (M.D.A.T. 1982)

16. Which of the following salt is insoluble in water at room temperature but soluble in hot water ?
(1) $CaCl_2$ (2) $BaCl_2$ (3) $SrCl_2$ (4) $PbCl_2$ (5) $MgCl_2$. (P.M.D.T. 1978)

17. Pb_3O_4 on heating gives
(1) $PbO+O_2$ (2) $PbO+O_3$ (3) PbO_2+O_2 (4) PbO_2+O_2 (5) PbO_2 only. (P.M.D.T. 1979)

18. Lead Pencil contains
(1) Pb (2) FeS (3) Graphite (4) PbS. (I.I.T. 1980)

19. HCl is added to the following oxides. Which of them would give H_2O_2 ?
(1) MnO_2 (2) PbO_2 (3) BaO (4) NO_2 (5) None. (I.I.T. 1980)

20. Lead is most readily soluble in
(1) Acetic acid (2) Sulphuric acid
(3) Nitric acid (4) Hydrochloric acid.

21. Mark the compound which is used as an antiknock in petrol fuel.
(1) Lead tetra acetate (2) Basic lead sulphate .
(3) Lead tetra ethyl (4) Sublimed white lead.
(C.P.M.T. 1981)

22. Sugar of lead is

    (1) $2PbSO_4.PbO$ (2) $(CH_3COO)_2Pb$
    (3) $PbCO_3$ (4) $PbCO_3.Pb(OH)_2$.

23. Which of the following is liquid at room temperature ?

    (1) $SnCl_2$ (2) PbO (3) PbO_2 (4) $PbCl_2$ (5) $SnCl_4$.

24. Which of the following is obtained when $SnCl_2$ reacts with $HgCl_2$. ?

    (1) Hg (2) Hg_2Cl_2 (3) $HgCl$ (4) None.

25. Which of the following reacts with acid and base both ?

    (1) $SnCl_2$ (2) $SnCl_4$ (3) PbO_2 (4) SnO.

26. Which of the following metal reacts with $NaOH$ to give H_2 ?

    (1) Sn (2) Pb (3) Fe (4) Mg (5) More than one.

27. Which of the following is known as massicot ?

    (1) PbO (2) PbO_2 (3) Pb_3O_4 (4) $PbCrO_4$.

□□□

CHAPTER 19

IRON

Symbol—*Fe. At. No.* 26. *At. wt.* 55·847.

Electronic configuration : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

Occurrence :

Iron is the 4th most abundant element in the earth's crust and occurs to the extent of 50,000 p.p. m. It occurs free in nature only in meteorites. In the combined state it occurs as :

(i) *Haematite*, Fe_2O_3; (ii) *Magnetite*, Fe_3O_4; (iii) *Limonite*, $2Fe_2O_3.3H_2O$; (iv) *Siderite*, $FeCO_3$, (v) *Iron pyrites*, FeS_2.

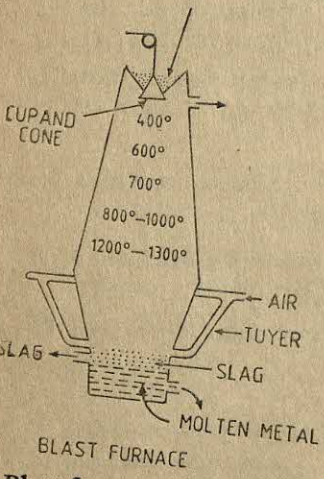
Forms of iron :

Three varieties of iron are usually prepared. These forms have different carbon contents. **Cast iron** or **Pig iron** contains 2 to 5 per cent of carbon, **Steel** 0·2 to 1·8 per cent of carbon and **Wrought iron** only 0·12 to 0·25 per cent of carbon. Besides this other impurities may be sulphur, phosphorus, silicon, manganese or traces of other elements. It is manufactured from **Haematite.**

Manufacture of Cast iron or Pig iron :

(i) **Concentration.** The powdered ore is concentrated by the gravity process to remove the lighter gangue particles.

(ii) **Roasting or Calcination.** The concentrated ore is then roasted or calcined in excess of air. Sulphur, phosphorus, arsenic, etc. are converted into oxides and are lost. Moisture is also driven off. Ferrous oxide is converted into ferric oxide. The loss of iron as slug during smelting is thus avoided as ferric oxide does not form a slag with silica at as low a temperature as ferrous oxide. As a result of calcination, the mass becomes porous which makes its reduction to iron during smelting easy.



Blast furnace for cast iron.

$$Fe_2O_3.3H_2O \rightarrow Fe_2O_3 + 3H_2O$$
$$4FeO + O_2 \rightarrow 2Fe_2O_3$$

(iii) **Smelting.** The roasted ore is mixed with coke (fuel and reducing agent) and lime stone (flux). This mixture is added at the top of a blast furnace and a blast of hot air is introduced at its base. The burning of coke furnishes the furnace, it is exposed to increasing temperatures which rise from about 400° – 600°C at the top to about 1500° – 1700°C at the bottom.

The following reactions take place in the blast furnace :

(i) **Top Zone or Reduction** (400° – 700°C)

Ascending carbon monoxide reduces iron oxide to a form known as spongy iron.

$$Fe_2O_3+3CO \rightarrow 2Fe+3CO_2$$
$$Fe_3O_4+4CO \rightarrow 3Fe+4CO_2$$
$$Fe_3O_4+2C \rightarrow 3Fe+2CO_2$$

(ii) **Middle Zone or Zone of Heat Absorption (800° – 1000°C)**

Lime stone decomposes to form lime which reacts with silica to form calcium silicate. This is removed as a fusible slag.

$$CaCO_3 \rightarrow CaO+CO_2$$
$$CaO+SiO_2 \rightarrow \underset{\text{slag.}}{CaSiO_3}$$

Carbon dioxide moving up passes over hot coke and is reduced to carbon monoxide which continues to move up.

$$CO_2+C \rightarrow 2CO.$$

Coke present in the charge burns to produce carbon dioxide. Since this reaction is exothermic, a lot of heat is produced here.

$$C+O_2 \rightarrow CO_2$$

The spongy iron moving down from above melts. Molten iron and slag collect at the bottom of the furnace and are removed separately.

Iron, thus obtained, contains 2-5% carbon and small amounts of *Si*, *P*, *S* and *Mn* and is called cast **iron** or **pig iron**. If the molten iron is cooled suddenly, a white crystalline variety called **white cast iron** is obtained. In this variety carbon is present in the form of *cementite*, Fe_3C. However, if the molten iron is cooled slowly, grey **cast iron** is obtained which contains carbon in the form of graphite.

White Cast iron. If the Pig iron is permitted to cool suddenly all the carbon remains present in it in the form of iron carbide or cementtite (Fe_3C) and the iron thus obtained is known as **white cast iron.**

Grey Cast iron. If the pig iron is cooled slowly, some of the carbon present in iron forms tiny flakes of graphite which impart greyish appearance to it. This is known as **Grey Cast iron.**

Grey cast iron is suitable for castings since it expands on solidification. It is a brittle and breaks easily when struck. It is used for casting machine frames, fly wheels, drainage pipes, electric lamp poles, plates, etc.

1. Cementation Process from wrought iron :

It is an old process for the manufacture of steel from wrought iron. Wrought iron bars packed with powdered charcoal and heated in sealed fire brick boxes at about 1000°C for a week. Carbon is gradually absorbed by the rods converting them into steel. The surface of the bars is covered with blisters and the steel formed is known as *Blister steel.* It is fused in crucibles to get crucible steel. It is now melted and spiegel (an alloy of iron, manganese and carbon) is added which gives steel of desired quality.

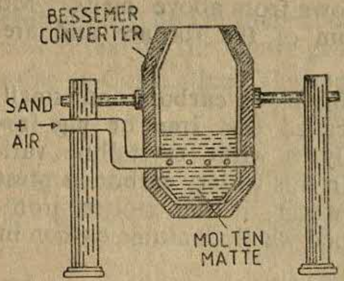
2. Manufacture of steel from cast iron :

(i) Bessemer's Process. Principle :

All the impurities present in the cast iron are removed by oxidation and then required quantity of spiegel are added to obtain steel.

In this process Bessemer's converter which is a pear-shaped furnace is used to convert cast iron into steel. The converter is made of iron and lined inside with silica (acid-lining) or dolomite, $MgCO_3$, $CaCO_3$ (basic-lining). It can hold up to 40 to 50 tons of pig iron at a time and is mounted on trunnious so that it is capable of being tilted in any position.

The molten pig iron from the blast furnace is transferred to the converter while it is in the horizontal position. It is then gradually raised to the vertical position and hot air blast is passed through the tuyers. The bottom of the converter has a large number of small holes through which air enters into the entire mass of the pig iron and oxidises its impurities. Silicon and manganese are first oxidised and pass into the slag.



Bessemer converter

$$Si+O_2 \rightarrow SiO_2$$
$$2Mn+O_2 \rightarrow 2MnO$$
$$MnO+SiO_2 \rightarrow MnSiO_3$$

Sulphur combines with oxygen to form sulphur dioxide which volatilizes away, carbon is oxidised to carbon monoxide which burns as a blue flame at the mouth of the converter. When its flame sinks, it indicates that all the carbon has been burnt way and the converter contains pure wrought iron. The operator can judge from the colour of the flame as to when to cut off the supply of air blast. Then speigel is added in the molten mass to obtain steel of the desired quality. It is uniformly distributed by blowing air through it for few minutes. The entire process lasts for about 10-12 hours, after which the product is withdrawn from the converter by tilting.

When the cast iron contains much of phosphorus then it is not possible to remove it by using a converter lined with silica. It is then removed by **Basic Bessemer's Process** where the converter is lined with basic lining of magnesia and lime and little lime stone.

In this process first silicon and manganese form oxides which collect as slag. When the flame of carbon dioxide sinks then spiegel is added.

The phosphorous is oxidised to phosphorous pentoxide which combines with lime or magnesia to form calcium and magnesium phosphates which collect as slag. Thig slag must be completely removed before the addition of spiegel.

$$4P+5O_2 \rightarrow 2P_2O_5$$
$$P_2O_5+3CaO \rightarrow Ca_3(PO_4)_2$$
$$P_2O_5+3MgO \rightarrow Mg_3(PO_4)_2$$

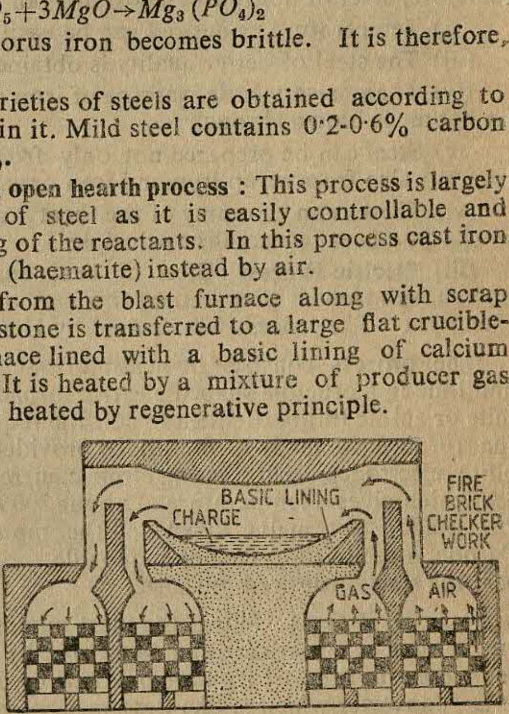
In presence of phosphorus iron becomes brittle. It is therefore, essential to remove it.

Note : (i) Different varieties of steels are obtained according to the percentage of carbon in it. Mild steel contains 0·2-0·6% carbon and tool steel 0·6 to 1·5%.

(ii) **By Siemen Martin open hearth process** : This process is largely used for the manufacture of steel as it is easily controllable and there is an efficient mixing of the reactants. In this process cast iron is purified by ferric oxide (haematite) instead by air.

The molten cast iron from the blast furnace along with scrap iron, haematite and lime stone is transferred to a large flat crucible-shaped hearth of the furnace lined with a basic lining of calcium and magnesium oxides. It is heated by a mixture of producer gas and air. This mixture is heated by regenerative principle.

The charge consists of 80% cast iron, 20% wrought iron, scrap iron and haematite, is taken in an open hearth lined with basic lining. It is heated by a mixture of producer gas and air which works on regenerative principle of heat economy.



Open Hearth Furnace

Reaction in the Open Hearth Process :

Carbon and sulphur react with haematite to form carbon monoxide and sulphur dioxide which are evolved out.

$$Fe_2O_3+3C\rightarrow 2Fe+3CO$$
$$2Fe_2O_3+3S\rightarrow 4Fe+3SO_2$$

Phosphorous and silicon also give acidic oxides which form slag. Manganese if present also forms slag.

$$5Fe_2O_3+6P\rightarrow 10Fe+3P_2O_5$$
$$2Fe_2O_3+3Si\rightarrow 4Fe+3SiO_2$$
$$P_2O_5+3CaO\rightarrow Ca_3(PO_4)_2 \text{ (Slag)}$$
$$SiO_2+CaO\rightarrow CaSiO_3 \text{ (Slag)}$$
$$Fe_2O_3+3Mn\rightarrow 2Fe+3MnO$$
$$MnO+SiO_2\rightarrow MnSiO_3 \text{ (Slag)}$$

Advantages over Bessemer's Process :

The open hearth process is more perfect. It has the following advantages :

(i) Steel samples can be examined from time to time and therefore, steel of desired composition can be prepared.

(ii) Temperature as desired can be easily maintained.

(iii) The steel of better quality is obtained.

(iv) There is very little wastage of iron as slag in this process as no hot air is blown through it.

(v) Steel can be prepared not only from pig iron or wrought iron but also from scrap iron and iron ores.

(vi) There is an economy of the heat i.e. fuel as the furnace works on a heat regenerative principle.

(iii) Electric Process : Steel of best quality free from sulphur and phosphorous is prepared by this method though the method is expensive. The process was devised by **Heroilt.**

The process consists in heating Bessemer's steel, some iron ore and lime in a crucible shaped electric furnace lined inside with dolomite or acidic lining of silica to suit the requirement. The roof of the furnace is made of fire bricks provided with water-cooled graphite electrodes. On passing electric current, electric arc is produced which gives a temperature of about 2000°C or even higher. The low grade steel melts down and the impurities pass into the slag. Carbon is removed as carbon monoxide. Spiegel is added to prepare the steel of desired purpose.

(iv) L. D. Process : This is the most modern method developed by the German scientist *Linz* and *Downwitz*. In this method the impurities present in the cast iron are oxidised by oxygen. In this method L. D. converter which is like Bessemer converter is used, but there are no air holes in its bottom. There is a pipe known as *oxygen lens* for passing pure oxygen in the converter. A hopper is provided to add limestone. The process takes about 25 minutes for completion. The steel is prepared by this method at Rourkela in Orissa. Cast iron is smelted down in the furnace and oxygen under pressure is passed in. Impurities are oxidised and collect on the surface as slag which is removed. Spiegel is added to prepare steels of desired qualities.

Properties of iron :

Physical properties :

Pure iron is silvery white and soft metal, m. p. 1528°C. It is easily magnetised when placed inside a coil carrying an electric current, but loses its magnetism when the current is switched off.

Allotropy :

Iron exhibits *allotropy*. The stable form of iron at ordinary temperature is the α-form (also known as ferrite) which is ferro-magnetic and possesses a body centred cubic lattice. At 768°C (the Curie point) the α-form ceases to be magnetic and at this point the iron is known as the β-iron, which possesses the same crystalline structure as the α-form. At 906°C, the iron has a face-centred cubic form (γ-iron) and at 1401°C to the body-centred cubic structure again (δ-iron)

$$Fe\alpha \overset{768°C}{\rightleftharpoons} Fe\beta \overset{906°C}{\rightleftharpoons} Fe\gamma \overset{1401°C}{\rightleftharpoons} Fe\delta.$$

Chemical properties :

1. *Action of air* : Dry air has got no effect on iron. When exposed to air and moisture, iron gets rapidly oxidised to a *hydrous oxide*, known as *rust of iron*. Although the composition of the rust varies somewhat it consists mainly of hydrated iron oxide, $2Fe_2O_3.3H_2O$, together with a small quantity of iron (11) carbonate.

2. *Action of water* : Iron displaces hydrogen from steam at high temperatures.

$$3Fe + \underset{\text{Redhot steam}}{4H_2O} \rightarrow Fe_3O_4 + 4H_2$$

3. *Action of alkalies* : Iron does not react with alkalies.

4. *Action of acids* : Since oxidation potential of the reaction

$$Fe \rightarrow Fe^{+2} + 2e$$

is positive, being +0·44 volt, iron dissolves in dilute hydrochloric acid or sulphuric acid liberating hydrogen.

$$Fe + 2HCl \rightarrow FeCl_2 + H_2\uparrow$$
$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2\uparrow$$

It also dissolves in *dilute nitric acid*, forming ammonium nitrate.

$$4Fe + 10HNO_3 \rightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$$

When placed in *highly concentrated nitric acid*, it becomes *passive* i.e. it loses its normal reactivity probably due to the formation of a layer of insoluble and impervious oxide over iron surface.

5. *Combination with non-metals* : Iron combines directly with chlorine and other halogens on heating. It also combines with other non-metals like S, P, B, C and Si at high temperature.

$$2Fe+3Cl_2 \rightarrow 2FeCl_3$$
$$3Fe+4Br_2 \rightarrow Fe_3Br_8$$
$$Fe+S \rightarrow FeS$$

6. *Action of Carbon Monoxide* : When CO gas is passed over heated Fe at 120°C, iron carbonyl, $Fe(CO)_5$, is formed.

$$Fe+5CO \rightarrow Fe(CO)_5$$

7. *Replacement of metals* : Iron will replace, form solutions of thin salts, metals below it in the electrochemical series e.g.

$$CuSO_4+Fe \rightarrow FeSO_4+Cu$$
$$Fe+Cu^{2+} \rightarrow Cu+Fe^{2+}$$

8. *Electronic configuration and oxidation states* : The outer electronic configuration of iron is $3d^6\,4s^2$. It shows oxidation states of 0, +2, +3, +4, +5 and +6 but only +2 and +3 states are common. The zero oxidation state occurs in the case of carbonyls where the bonding electrons are contributed by CO molecules. The +2 state is caused by the removal of the two $4s$-electrons. The +3 state involves removal of one of the $3d$-electrons as well. This takes place easily since this leaves an *exactly half-filled 3d-subshell* ($3d^5$ configuration) which, therefore, is highly stable. The iron (III) ion Fe^{3+}, therefore, is highly stable. The oxides are good catalysts on account of their fine state of sub-division and hence large surface area per gram.

Passive iron :

When a piece of iron is lowered in conc. HNO_3, chloric acid, chromic acid, potassium permanganate or silver nitrate solution then it becomes passive.

Passive iron returns to the normal state when heated in a reducing atmosphere of hydrogen or carbon monoxide or immersed in a concentrated solution of an alkali.

Passivity of iron is believed to be due *to formation of an extremely thin* (almost imperceptible) and *impervious film of ferroso-ferric oxide, Fe_3O_4, on the surface of iron*. The reaction of iron with the acid, therefore, slows down considerably to such an extent that it cannot be detected. This view receives support from the fact that the passivity is removed by scratching or by dissolving out the iron oxide in iodine solution. The passivity of iron is important in preventing corrosion of iron.

19.1. Compounds of Iron :

Oxides of Iron

Three oxides of iron, namely, *iron (II) oxide*, FeO, *iron (III) oxide*, Fe_2O_3 and *(II)-iron (III)* oxide, Fe_3O_4 which is a double compound of the first two oxides, are known. All the three oxides, on treatment with hydrogen, are reduced to give the metal.

All the three oxides have essentially a *related structure.* This structure may be regarded as a *cubic close-packed, array of oxide ions with metal ions* (Fe^{2+} and Fe^{3+}) fitting into the *octahedral* and *tetrahedral interstices*.

1. Iron (II) Oxide, Ferrous oxide, FeO :

It is obtained as a black powder, contaminated with ferroso-ferric oxide (Fe_3O_4) and carbon, by heating iron (II) oxalate.

$$FeC_2O_4 \rightarrow FeO + CO\uparrow + CO_2\uparrow$$

It is also obtained by reducing iron (III) oxide in a current of hydrogen.

$$Fe_2O_3 + H_2 \rightarrow 2FeO + H_2O$$

It is stable only at high temperature. On cooling it decomposes to give ferroso-ferric oxide and iron.

$$4FeO \rightarrow Fe_3O_4 + Fe$$

It is basic in nature and gives iron (II) salts on treatment with dilute acids.

$$FeO + 2HCl \rightarrow FeCl_2 + H_2O$$
$$FeO + H_2SO_4 \rightarrow FeSO_4 + H_2O$$

It is oxidised to give ferric oxide.

2. Iron (III) oxide, Ferric oxide, Fe_2O_3 :

Preparation. :

It occurs naturally in the ores as *haematite* and *limonite.* In laboratory, it may be prepared by strongly heating iron (II) sulphate.

$$2FeSO_4 \rightarrow Fe_2O_3 + SO_2 + SO_3$$

It can also be obtained by heating ferric hydroxide.

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$$

Properties : It is ionic in nature. It shows amphoteric character [cf. iron (II) oxide is basic]. It reacts with acids to form iron (III) salts and with alkalies to give ferrites.

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O$$
$$Fe_2O_3 + 2NaOH \rightarrow \underset{\text{Sod. Ferrite}}{2NaFeO_2} + H_2O$$

Sodium ferrite is unstable and gives hydrated iron (III) oxide on dilution.

Iron (III) oxide is reduced to iron (II) oxide when heated in hydrogen or carbon monoxide. It is known as *Jewellers rouge.*

Uses : It is used (a) as a red pigment, (b) as a metal polish, (c) as a catalyst in Bosch Process.

3. Iron (II)-iron (III) oxide, Ferrosoferric oxide, magnetic oxide of iron, Fe_3O_4 :

Preparation : (i) By passing steam over red hot iron or by quenching red hot iron in water.

$$3Fe+4H_2O \rightarrow Fe_3O_4+4H_2$$

Properties. It is more stable than the other two oxides of iron. It has magnetic properties. It resists the action of chlorine, acids and oxygen and is therefore, used as an anode in electrolytic process.

It dissolves *slowly* in acids giving a mixture of iron (II) and iron (III) salts.

$$Fe_3O_4+8HCl \rightarrow 2FeCl_3+FeCl_2+4H_2O.$$
$$(Fe_3O_4+8H^+ \rightarrow Fe^{2+}+2Fe^{3+}+4H_2O)$$

4. Anhydrous Ferrous chloride, $FeCl_2$:

It is formed as colourless ferrous chloride crystals in the receiver when iron wire is heated with hydrogen chloride gas in a hard tube. The receiver is kept out of contact of air.

Properties : (i) Anhydrous salt forms deliquescent, colourless crystals which are soluble in water. The hydrated salt is of green colour. Both are soluble in acids.

(ii) It is oxidised to ferric chloride when chlorine is passed through its aqueous solution.

$$2FeCl_2+Cl_2 \rightarrow 2FeCl_3$$

(iii) On heating in air it forms ferric oxide and ferric chloride.

$$12FeCl_2+3O_2 \rightarrow 2Fe_2O_3+8FeCl_3$$

(iv) When steam is passed over it, Fe_3O_4 is formed.

$$3FeCl_2+4H_2O \rightarrow 6HCl+Fe_3O_4+H_2$$

It absorbs ammonia and nitric oxide to form complex salts $FeCl_2.6NH_3$ and $FeCl_2.NO$ respectively.

5. Anhydrous Ferric chloride, $FeCl_3$ Or Fe_2Cl_6 :

Preparation :

It is prepared by passing dry chlorine over heated iron wire or ferric oxide. The temperature of iron is maintained at 900°C to 1000°C when ferric chloride sublimes over as yellowish red crystalline mass.

$$2Fe+3Cl_2 \rightarrow 2FeCl_3$$
$$2Fe_2O_3+6Cl_2 \rightarrow 4FeCl_3+3O_2$$

Properties : 1. The anhydrous chloride is black and hydrated form is yellow. Both forms are soluble in water and give acidic solution due to hydrolysis.

$$FeCl_3+3H_2O\rightarrow Fe(OH)_3+3HCl$$

2. On heating the hydrated form ferric oxide is formed while the anhydrous salt gives ferrous chloride and chlorine.

$$FeCl_3.6H_2O\rightarrow FeCl_3.3H_2O+3H_2O$$
$$2FeCl_3.3H_2O\rightarrow 6HCl+Fe_2O_3$$
$$2FeCl_3\rightarrow 2FeCl_2+Cl_2$$

3. Ferric chloride acts as an oxidising agent and is itself reduced to ferrous salts when it reacts with hydrogen sulphide, stannous chloride or hydrogen.

$$2FeCl_3+H_2S\rightarrow 2FeCl_2+2HCl+S$$
$$2FeCl_3+SnCl_2\rightarrow 2FeCl_2+SnCl_4$$
$$2FeCl_3+H_2\rightarrow 2FeCl_2+2HCl$$
$$2FeCl_3+2KI\rightarrow 2FeCl_2+2KCl+I_2$$

Its vapour density at 440°C corresponds with the molecular formula Fe_2Cl_6 and to $FeCl_3$ at 750°C. Hydrates of ferric chloride containing 12, 7, 5 and 4 molecules of water of crystallization, are known.

Uses : 1. It prevents bleeding as it coagulates blood.

2. It is used as a laboratory reagent.

3. It is used in medicines. Its alcoholic solution is known as Tincture Ferric Perchloride.

6. Ferrous sulphate or Green vitriol, $FeSO_4.7H_2O$:

It is obtained by the action of dilute sulphuric acid on iron, ferrous oxide, ferrous sulphide or ferrous carbonate and evaporating the solution to crystallization when crystals of $FeSO_4.7H_2O$ are obtained.

$$Fe+H_2SO_4\rightarrow FeSO_4+H_2\uparrow$$
$$FeO+H_2SO_4\rightarrow FeSO_4+H_2O$$
$$FeS+H_2SO_4\rightarrow FeSO_4+H_2S$$
$$FeCO_3+H_2SO_4\rightarrow FeSO_4+H_2O+CO_2$$

It is obtained in the laboratory as a bye product during the preparation of hydrogen sulphide by Kipp's apparatus.

Manufacture : On commercial scale ferrous sulphate is prepared roasting iron pyrites in heaps and exposing them to the action of air and water.

$$2FeS_2+7O_2+2H_2O\rightarrow 2FeSO_4+2H_2SO_4$$

It is extracted with water and iron fillings are added to the filtrate. Thus sulphuric acid present in the filtrate changes to ferrous sulphate. Besides any ferric sulphate formed is also reduced to ferrous sulphate by nascent hydrogen.

$$Fe+H_2SO_4\rightarrow FeSO_4+2H$$
$$Fe_2(SO_4)_3+2H\rightarrow 2FeSO_4+H_2SO_4$$

The solution on concentration gives crystals of $FeSO_4.7H_2O$.

Properties : (i) It forms light green crystals, soluble in water. It is an efflorescent substance. On heating it loses its water of crystallization and decomposes into ferric oxide, sulphur dioxide and sulphur trioxide.

$$FeSO_4.7H_2O\xrightarrow{140°C}FeSO_4.H_2O\xrightarrow{300°C}FeSO_4+H_2O$$
$$2FeSO_4\longrightarrow Fe_2O_3+SO_2+SO_3$$

(ii) When exposed to air, the crystals turn brown due to the formation of basic ferric sulphate.

$$4FeSO_4+2H_2O+O_2\rightarrow 4Fe(OH)SO_4$$

(iii) It dissolves in nitric oxide to form a dark brown solution of nitroso ferrous sulphate which is an unstable substance.

$$FeSO_4+NO\rightarrow FeSO_4.NO$$

(iv) It is hydrolysed by water giving acidic solution.

$$FeSO_4+2H_2O\rightarrow Fe(OH)_2+H_2SO_4$$

(v) It is oxidised to ferric sulphate by air or other oxidising agent.

$$2FeSO_4+H_2SO_4+\text{'O'}\rightarrow Fe_2(SO_4)_3+H_2O$$

(vi) *Reducing Properties* : Ferrous sulphate is a good reducing agent. It decolourises acidified potassium permanganate solution and acidified potassium dichromate solution is turned green.

$$2KMnO_4+3H_2SO_4\rightarrow K_2SO_4+2MnSO_4+3H_2O+5\text{'O'}$$
$$\underline{10FeSO_4+5H_2SO_4+5[O]\rightarrow 5Fe_2(SO_4)_3+5H_2O}$$
$$2KMnO_4+8H_2SO_4+10FeSO_4\rightarrow K_2SO_4+2MnSO_4+5Fe_2(SO_4)_3+8H_2O$$

(vii) It forms double salts with alkali metals or ammonium sulphate, e.g. ferrous ammonium sulphate, $FeSO_4.(NH_4)_2SO_4\,6H_2O$ (Mohr's salt).

Uses : 1. As an antiseptic it is widely used in agriculture.

2. In the manufacture of blue-black ink.

3. As a mordant in dyeing.

4. As a laboratory reagent.

7. Ferrous Ammonium Sulphate,
Mohr's salt, $FeSO_4(NH_4)_2SO_4.6H_2O$:

Preparation : When a solution containing equimolar proportions of ferrous sulphate and ammonium sulphate is evaporated, a double salt, $FeSO_4(NH_4)_2SO_4.6H_2O$ crystallises out. This is called *Mohr's salt*.

Properties : It is greenish solid, soluble in water. It is acidic in nature. It acts as a reducing agent. It reduces acidified $KMnO_4$, $K_2Cr_2O_7$ solution and $AuCl_3$ etc.

(i) *Reaction with* $KMnO_4$: It reacts with $FeSO_4$ to give ferric sulphate and $MnSO_4$ in presence of dil. H_2SO_4.

$$\begin{array}{l}
\quad 2KMnO_4 \rightarrow K_2O + 2MnO + 5\text{'}O\text{'} \\
\quad K_2O + H_2SO_4 \rightarrow K_2SO_4 + H_2O \\
\quad 2MnO + 2H_2SO_4 \rightarrow 2MnSO_4 + 2H_2O \\
\quad 10FeSO_4 + 5H_2SO_4 + 5\text{'}O\text{'} \rightarrow 5Fe_2(SO_4)_3 + 5H_2O \\
\hline
2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \\
\qquad \rightarrow 2MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + 8H_2O
\end{array}$$

$$(10Fe^{2+} + 2MnO_4^{-1} + 16H^{+} \rightarrow 2Mn^{2+} + 10Fe^{2+} + 8H_2O)$$

(ii) *Reaction with* $K_2Cr_2O_7$: It reacts with $K_2Cr_2O_7$ solution which is turned green :

$$\begin{array}{l}
\quad K_2Cr_2O_7 \rightarrow K_2O + Cr_2O_3 + 3\text{'}O\text{'} \\
\quad K_2O + H_2SO_4 \rightarrow K_2SO_4 + H_2O \\
\quad Cr_2O_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3H_2O \\
\quad 6FeSO_4 + 3H_2SO_4 + 3\text{'}O\text{'} \rightarrow 3Fe_2(SO_4)_3 + 3H_2) \\
\hline
K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \\
\qquad \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 3Fe(SO_4)_3 + 7H_2O
\end{array}$$

$$(Cr_2O_7^{-2} + 6Fe^{2+} + 14H^{+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O)$$

(iii) *Reaction with auric chloride,* $AuCl_3$:

$$AuCl_3 + 3FeSO_4 \rightarrow FeCl_3 + Fe_2(SO_4)_3 + Au$$

Uses : It is used in permanganate titration.

8. **Hydrated Iron (III) sulphate, Ferric sulphate,** $Fe_2(SO_4)_3\ 9H_2O$ **:**

Preparation : By the oxidation of ferrous sulphate in sulphuric acid solution by H_2O_2, HNO_3 or even concentrated sulphuric acid.

$$2FeSO_4 + 2H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 5O_2 + 2H_2O$$

$$2FeSO_4 + H_2SO_4 + H_2O_2 \rightarrow Fe_2(SO_4)_3 + 2H_2O$$

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

On crystallisation of the solution, crystals of $Fe_2(SO_4)_3.9H_2O$ separate out.

Properties : It decomposes readily on heating.

$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_2.$$

It forms alum, the best known being ammonium iron (III) sulphate, $NH_4Fe(SO_4)_2.12H_2O$.

19.2 Tempering of Steel

When steel is heated and the red hot steel is dipped in a liquid to cool, steel becomes very hard. This process is called *tempering of steel.* The hardness of tempered steel depends on

(a) its carbon content. (b) the mode of cooling of the red hot steel, (c) the rate of cooling.

If red hot steel is quickly plunged into oil, it becomes hard and brittle like glass.

Tempered Steel and their uses

Temperature	*Colour of oxide layer on the surface of steel*	*Use*
220°C	Light yellow	For making blades.
255°C	Brownish yellow	For making knives and axes
277°C	Pinkish	For making knives and scissors.
288°C	Bright blue	For making spring for watches and sword.
290°C	Deep blue	For making saws and other cutting tools.

19.3. Annealing

If steel is heated at high temperatures and then it is slowly cooled, the hardness of steel decreases. This process is called **annealing.**

The quality of annealed steeldepends on the temperature to which steel is heated and the process by which it is cooled. If the steel is heated to high temperatures and cooled slowly, the softness of steel increases.

19.4. Distinguishing Tests Between Ferrous and Ferric Salts

Test	*Ferrous salt*	*Ferric salt*
1. Colour	Light greenish white	Yellow or brown.
2. Colour of solution	Nearly colourless	Yellow.
3. With NH_4OH, $NaOH$ or KOH solution	Light green ppt. of $Fe(OH)_2$	Reddish brown ppt. of $Fe(OH)_3$.
4. On adding ferric-cyanide solution	A white ppt. of pot. ferrous ferrocyanide, $K_2[Fe(CN)_6]$ is formed which turns blue in air.	A dark blue ppt. of ferric ferrocyanide $Fe_4[Fe(CN)_6]$ (Prussian blue) is formed,
5. Salt solution + pot ferricyanide solution	A dark blue ppt. of ferrous ferricyanide $Fe_3Fe(CN)_6$ (Turn bulls blue) is formed.	No ppt. is formed only reddish brown colouration is Produced.
6. Salt solution + ammonium sulphocyanide	No reaction.	A blood red colouration of ferric sulphocyanide $Fe(CNS)_3$ is formed.

19.5. Analytical Tests for Iron

(i) A ferrous salt is oxidised to ferric salt by heating with concentrated nitric acid. If no ammonium hydroxide is added to it then a reddish brown precipitate of ferric hydroxide is obtained.

$$FeCl_3+3NH_4OH \rightarrow Fe(OH)_3+3NH_4Cl$$

(ii) If the above precipitate is dissolved in dilute hydrochloric acid and potassium ferrocyanide solution is added, a dark blue precipitate (Prussian blue) is obtained.

(iii) If the precipitate is dissolved in dilute hydrochloric acid and few drops of ammonium sulphocyanide, NH_4CNS solution is added, a blood red colouration is obtained.

(iv) Iron salts produce pale green colour to borax bead in reducing flame and yellow colour in oxidising flame.

Exercises

Long type question :

1. (a) Write names and chemical formulae of any three important ores of iron.
   (b) Draw a neat labelled diagram of the blast furnace that is used for the extraction of iron.
   (c) Explain with equations the various reactions that takes place in the blast furnace.
2. Give the names and formulae of three commonly occuring ores of iron which are of economic importance.
   Discuss the reactions which occur in the blast furnace during the manufacture of pig iron. What are the essential difference between cast iron, wrought iron and steel ?
3. Write down the electronic configuration of iron. What are the main differences between pig iron, wrought iron and steel ? Starting from iron, how would you prepare ferrous sulphate and anhydrous ferric chloride ? **(M. U. 1981)**
4. How would you prepare the following ?
   (a) Anhydrous ferric coloride.
   (b) Mohr's salt. (c) Green vitriol.
5. Give names and formulae of two important ores of iron. Disuss the principles involved in the extraction of pig iron from one of the ores of iron. How would you distinguish between Fe^{+2} and Fe^{+3} salts ? Write a note on rusting of iron. **(B. I. E. C. 1985)**
6. How will you obtain the following from iron ?
   (a) Ferric chloride, (b) Green vitriol, (c) Fe_3O_4. **(M. U. 1973)**
7. What happens when
   (1) a blade of iron is dipped in $CuSO_4$ solution ? **(P. U. 1974A)** (2) potassium ferricyanide solution is added to solution of ferrous sulphate ? **(P. U. 1974 A)** (3) $FeSO_4$ reacts with acidified $KMnO_4$ solution. (4) $FeSO_4$ reacts with acidified $K_2Cr_2O_7$ solution ? (5) Steam is passed over red hot iron ?

(6) $SnCl_2$ solution is added to $FeCl_3$ solution? (7) SO_2 passed in $FeCl_3$ solution (I. I. T. 1968 A) (8) H_2S is passed in $FeCl_3$ solution (I. I. T. 1968 A) (9) Fe_2O_3 reacts with $NaOH$ (10) $FeCl_3$ reacts with $FeSO_4$ solution ? (11) $AuCl_3$ reacts with $FeSO_4$ solution ? (12) $FeSO_4$ reacts with mixture of H_2SO and HNO_3 ? (12) Zn granules are added to acidified ferric sulphate solution) ? (I.I.T. 1968)

8. Write notes on—
   (1) Passivity of iron (**P. U. 1974 S**) (2) Tempering of steel (P. U. 1974 A) (3) Annealing.
9. Explain the following—
   (i) Sn^{+2} and Fe^{+3} iron cannot co-exist in solution. (I. I. T. 1967A)
   (ii) A little H_2SO_4 is added to $FeSO_4$ while preparing its solution. (I. I. T. 1972 A)
   (iii) A ferrous salt turns brown in air.
   (iv) Copper implements were known to mankind much earlier than iron implements.
   (v) Iron implements gets rusted in moist air.
   (vi) A ferrous salt solution decolourises acidifed $KMnO_4$ solution.
   (vii) A little HCl solution is always added to $FeCl_3$ solution while preparing its aqueous solution.
   (viii) An iron blade turns blue solution of copper sulphate colourless.
   (ix) In the metallurgy of iron, lime stone is added to the ore. (I. I. T. 1976 B)
10. State the essential steps and conditions for the extraction of iron from red haematite ore....... (I. I. T. 1968 B)
11. Fill up the blanks.
   (i) A solution of $FeCl_3$ in water is.........
   (ii) Green vitriol is an.........substance.
   (iii) Haematite is an ore of.........
   (iv) Iron oxide is used as.........rouge.
   (v) The magnetic oxide of iron has the formula......

Short type Questions

12. In the following reactions indicate (i) the element oxidised, (ii) element reduced, (iii) total no. of electrons transferred.

$$3Fe_3O_4+8Al\rightarrow 4Al_2O_3+9Fe \qquad \text{(I. I. T. 1975 A)}$$

(**Hint**. 24 electrons have been transferred from 8 atoms of Al to 9 atoms of iron.)

13. Write the reactions involved in the manufacture of steel by (i) Bessemer Convertor process (ii) Open Hearth process. (I. S. C. 1980)
14. Write down the formula of the compounds—
   (i) Green vitriol (ii) Mohr's salt (iii) Magnetite (iv) Ferric alum (v) Iron pyrites (vi) Rouge (vii) Ferric chloride (anhydrous).
15. Fill up the blank and balance the following reactions—
   (a) $Fe_3O_4+CO\rightarrow FeO+CO_2$ (I. I. T. 1978)
   (b) $FeSO_4\rightarrow Fe_2O_3+$.........$+$......... (I. I. T. 1977 gr)
   (c) $FeS+O_2\rightarrow Fe_2O_3+$......... (I. I. T. 1977 gr to B '76 A)
   (d) $Fe^{++}+NO_3^-+H^+\rightarrow Fe^{3+}$.........$+H_2O$ (I. I. T. 1976 gr B)
   (e) $Fe^{++}+H^++MnO_4^{-1}\rightarrow Fe^{+3}+H_2O+Cr^{3+}$

(f) $FeCl_3+H_2S \rightarrow FeCl_2+HCl+S$ **(I. I. T. 1973 gr B)**
(g) $FeCl_3+SnCl_2 \rightarrow FeCl_2+$.........
(h) $FeCl_3+K_4[Fe(CN)_6] \rightarrow 12KCl+$.........
(i) $FeCl_3+NH_4CNS \rightarrow NH_4Cl+$.........
(j) $Fe_2(SO_4)_3 \rightarrow Fe_2O_3+$.........
(k) $FeSO_4+H_2SO_4+HNO_3 \rightarrow Fe_2(SO_4)_3+$.........$+$.........

Select and write Correct answer for the following.

16. Fe^{2+} ion contains
(1) $3d^2$ electrons (2) $3d^4$ electrons (3) $3d^6$ electrons (4) $3d^5$ electrons.

17. Fe^{3+} ion contains.
(1) $3d^5$ electrons (2) $3d^3$ electrons (3) $3d^4$ electrons (4) $4s^2$ electrons.

18. Fe (atomic number 26) atom has the electronic arrangement
(1) 2, 8, 8, 8 (2) 2, 8, 16 (3) 2, 8, 14, 2 (4) 2, 8, 12, 4. **(N. C. E. R. T. 1974)**

19. Galvanised iron is protected from rusting because it has a coating of
(1) Mercury (2) Tin (3) Zinc (4) Chromium. **(N. C. E. R. T 1980)**

20. Iron is obtained on large scale from Fe_2O_3 by
(1) passing hydrogen (c) Calcination (3) reduction with Al (4) Reduction with carbon. **(C. P. M. T. 1979)**

21. Purest form of iron is
(1) White cast iron (2) Grey cast iron (3) wrougt iron (4) steel. **(C. P. M. T. 1980)**

22. Iron is manufactured from the ore
(1) Cryolite (2) Bauxite (3) Haematite (4) Chalcopyrites. **(C. P. M. T. 1979)**

23. Mohr's salt is
(1) simple salt (2) normal salt (3) complex salt (4) double salt.

24. Iron gets rusted by the action of
(1) Air (2) Air and water (3) Air, water and CO_2 (4) Air and CO_2.

25. Steel is heated to a bright red heat and then cooled slowly. It is
(1) Hardening (2) Annealing (3) Tempering (4) Nitriding.

26. The most stable oxidation state of iron is
(1) $+2$ (2) $+3$ (3) -2 (4) $+1$.

27. Railway wagon axles are made by heating rods of iron embedded in charcoal powder. The process is known as
(1) Tempering (2) Annealing (3) Case hardening (4) Sherardzing. **(C. P. M. T. 1980)**

28. Which of the following ore of iron contains carbon ?
(1) Siderite (2) Magnetite (3) Haematite (4) Red Haematite.

29. Iron is
(1) a normal element (2) a typical element (3) a transitional element (4) an inert element.

30. $FeSO_4.7H_2O$ is also known as
(1) Vermillion (2) Glauber's salt (3) Green vitriol (4) Mohr's salt.

31. Invar is an alloy of
(1) Fe and Ni (2) Fe, W, C (3) $Fe. Cr, Ni$ (4) Fe, Mn.

32. Which of the following variety of iron contains the least amount of carbon ?
(1) Pig iron (2) Cast iron (3) Wrought iron (4) none of these.

□□□

APPENDIX-1

Name of Processes

	Substances	*Processes*	*Materials used*
1.	H_2	Lane	Fe, H_2O (steam)
2.	H_2	Bosch	C, steam, Fe_2O_3 (catalyst), Cr_2O_3 (promoter)
3.	O_3 (Ozone)	Siemen's ozoniser	O_2
4.	O_3	Brodie's ozoniser	O_2
5.	Air	Claude	Air
6.	Argon	Linde's method	Liquid air
7.	White P_4	Retort	Bone, C, H_2SO_4 (conc.)
8.	S	Sicillian	From S-ore
9.	S	Frasch	From S-ore
10.	Cl_2	Deacon	HCl, air, $CuCl_2$ (catalyst)
11.	Cl_2	Down	Fused $NaCl$
12.	F_2	Moisson	KF in liquid HF
13.	F_2	Dennis	Electrolysis of KHF_2
14.	F_2	Whytlaw	KF
15.	Removal of temp. hardness	Clark	H_2O, $Ca(OH)_2$
16.	H_2O_2	E.Merck	Na_2O_2, H_2SO_4
17.	NH_3	Haber	N_2, H_2, Fe_2O_3 (catalyst) Mo (promoter)
18.	HNO_3	Chile saltpetre	$NaNO_3$, H_2SO_4
19.	HNO_3	Birkland Eyde	Air
20.	HNO_3	Ostwald	NH_3, O_2, Pt (catalyst)
21.	H_2SO_4	Lead chamber	SO_2, NO_2, oxides of N_2 as catalyst
22.	H_2SO_4	Contact	SO_2, NO_2, Pt or V_2O_5 as catalyst
23.	H_2SO_4 (conc^n)	Cascade	Dil. H_2SO_4
24.	H_2SO_4 (conc^n)	Gaillard	Dil. H_2SO_4
25.	Test for Arsenic	Gutzeit test	Arsenic to Arsine
26.	Na	Down	Fused $NaCl$, KF (flux)
27.	Na	Castner	Fused $NaOH$
28.	$NaOH$	Soda lime or Gossage	Lime stone and soda
29.	$NaOH$	Kellner-Solvay cell	$Ca(OH)_2$, $NaCl$
30.	$NaOH$	Castner-Kellner cell	Aq. $NaCl$
31.	$NaOH$	Nelson	Aq. $NaCl$
32.	$NaOH$	Lowig	Na_2CO_4 soln.
33.	$Na_2CO_3.10H_2O$	Leblanc	$NaCl$, $CaCO_3$, H_2SO_4
34.	$Na_2CO_3.10H_2O$	Solvay or Ammonia Soda	Saturated soln. brine ($NaCl$. NH_3, CO_2
35.	Ag	Parke	From Argentiferrous Lead
36.	Ag	Pattinson	From Argentiferrous Lead
37.	Purification of Ag	Cupellation	Impure Ag
38.	Au (Gold)	Mac-Arther Forest cyanide	Auriferrous quartz, KCN, air, water

Substances	*Processes*	*Materials used*
39. Zn	Silessian	ZnO, coke
40. Zn	Belgian	ZnO, coke
41. Zn	Vertical retort	ZnO, coke
42. Alumina from Bauxite	Hall's. Dry	Bauxite, Na_2CO_3
43. Alumina from Bauxite	Baeyer	Bauxite, $NaOH$
44. Alumina from Bauxite	Serpeck	Bauxite, C, N_2
45. Purification of Al	Hoop	Impure Al
46. Refining of Pb	Bettels Electrolytic	Impure lead
47. Bleaching Powder	Hesenclever	CaO, Cl_2, 40°C
48. Calcium nitride	Kaisser	Ca and N_2
49. Basic Lead carbonate	Dutch	Lead acetate
50. Basic Lead carbonate	Carter	Lead, acetic acid. CO_2
51. Concn. of sulphide ore	Froth floatation	Sulphide ore
52. As	Reinsch test	Test for Arsenic
53. Nickel	Mond	Extraction of Ni
54. Cast iron	Pyrometallurgy (Blast furnace)	Red Haematite, C, $CaCO_3$
55. Wrought iron	Puddling (Reverberators)	Scrap of iron or Red Haematite
56. Steel	Bessemer convertor	Pig iron and air
57. Steel	Siemens-Martin or open hearth	Pig iron or Scrap of iron; Producer gas
58. Steel	Duplex	Combination of 56 and 57 processes
59. Steel	L. D. (Linz-Donawitz)	Scrap of iron, Liquid O_2
60. K_2CO_3	Engel-Precht	KCl, $MgCO_3$, CO_2
61. Thermite welding	Goldschmidt	Welding

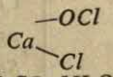
APPENDIX-2

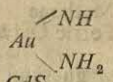
Name, Composition and Uses of Alloys

S.N.	*Name of Alloys*	*Composition of Alloys*	*Uses*
1.	Brass	$Cu=60-80\%$ $Zn=40-20\%$	Household utensils, cartridges
2.	Bronze	$Cu=75-90\%$ $Sn=25-10\%$	Utensils, coins and statues
3.	Phosphorous Bronze	$Cu=84{\cdot}75-92{\cdot}50\%$ $Sn=5{\cdot}15\%$ $P=0{\cdot}25-2{\cdot}5\%$	Radio aerial wire, galvanometer etc.
4.	German Silver or Nickel Silver	$Cu=50\%$ $Zn=25\%$ $Ni=25\%$	Utensils and decoration articles
5.	Gun-metal	$Cu=87\%$ $Sn=10\%$ $Zn=3\%$	Guns, gears, castings etc.
6.	Aluminium Bronze	$Cu=80-90\%$ $Al=7-12\%$ $Sn=0{\cdot}25-0{\cdot}5\%$	Coins, statue, golden paints, jewellery, cheap containers for corrosive liquids
7.	Monel metal	$Cu=30\%$ $Ni=67\%$ $Fe+Sn=3\%$	Acid pumps and containers for acids
8.	Bell metal	$Cu=80\%$ $Sn=20\%$	Bell, gongs etc.
9.	Magnelium	$Al=95\%$ $Cu=1{\cdot}75\%$ $Mg=2{\cdot}25\%$	Machine parts and cheap balances
10.	Duraluminium	$Al=95\%$ $Cu=4\%$ $Mn=0{\cdot}5\%$ $Mg=0{\cdot}5\%$	Airships
11.	Alnico	Steel$=50\%$ $Al=20\%$ $Ni=20\%$ $Co=10\%$	Permanent magnet
12.	Common Solder	$Sn=50-57\%$ $Pb=50-43\%$	Soldering broken articles
13.	Pewter	$Sn=75\%$ $Pb=25\%$	Utensils

S.N.	*Name of Alloys*	*Composition of Alloys*	*Uses*
14.	Y-alloy	$Al=92{\cdot}5\%$ $Mg=1{\cdot}5\%$ $Ni=2\%$ $Cu=4\%$	Aeroplane parts
15.	Britannia Metal	$Sn=93\%$ $Pb=5\%$ $Cu=2\%$	Spoons, forks
16.	Babbit Metal	$Sn=90\%$ $Sb=7\%$ $Cu=3\%$	Machinery
17.	Type Metal	$Pb=82\%$ $Sb=15\%$ $Sn=3\%$	Typewriter
18.	Antifriction Alloy	$Sn=75\%$ $Sb=12{\cdot}5\%$ $Cu=12{\cdot}5\%$	Bearing for machinery
19.	Newton Metal	$Pb=31\%$ $Sn=19\%$ $Bi=50\%$	Electric fuses, safety plugs
20.	Wood's Metal	$Pb=26\%$ $Sn=12{\cdot}5\%$ $Bi=50\%$ $Cd=12{\cdot}5\%$	Fusible alloy
21.	Nichrome	$Cr=8{\cdot}13\%$ $Ni=58-62\%$ $Fe=22{\cdot}25\%$ $Mn,\ Zn,\ SiO_2=1-2\%$ $C=0{\cdot}2-1\%$	Coils for electric furnaces
22.	Constatan	$Ni=40\%$ $Cu=60\%$	Electrical resistances
23.	Manganin	$Mn=12-15\%$ $Cu=82-84\%$ $Ni=2-4\%,\ Fe=1\%$	Resistance wires
24.	Rolled Gold	$Cu=80\%$ $Al=10-20\%$	Cheap ornaments
25.	Stainless Steel	$Ni=7-9\%$ $Cr=14-18\%$ $Fe=79-73\%$	Utensils, machine parts, tools etc.

Common Names, Chemical Names, Formulae, Uses

Common Name or Trade Name	*Chemical Name*	*Formula*	*Uses*
1. Alum	Hydrated potassium aluminium sulfate	$K_2SO_4.Al_2(SO_4)_3.24H_2O$	(i) Tanning of leather. (ii) Mordant in dyeing. (iii) Purification of water
2. Anglesite	Lead Sulfate	$PbSO_4$	Extraction of *Pb*
3. Alunite or Alumstone		$K_2SO_4Al_2(SO_4)_3.4Al(OH)_3$	,, *Al*
4. Argentite	Silver sulfide	Ag_2S	,, *Ag*
5. Bauxite	Hydrated aluminium oxide	$Al_2O_3.2H_2O$	,, *Al*
6. Baryta water	Barium hydroxide	$Ba(OH)_2.8H_2O$	Test for CO_2 and SO_2
7. Baking Soda	Sodium bicarbonate	$NaHCO_3$	In bakeries
8. Barytes or Heavy Spar	Barium sulfate	$BaSO_4$	Barium meal *X*-ray
9. Beryl	Beryllium aluminium silicate	$3BeO.Al_2O_3.6SiO_2$	Extraction of *Be*
10. Borax	Sodium borate deca hydrate	$Na_2B_4O_7.10H_2O$	Boric powder, Borax bead test, antiseptic
11. Bleaching powder	Calcium chloride, hypochlorite	 $Ca(OCl)Cl$	Germicide preparation of $CHCl_3$
12. Blue Vitriol	Copper sulfate pentahydrate	$CuSO_4.5H_2O$	Germicide, refining of crude *Cu*, electroplating
13. Butter of tin	Hydrated Stannic chloride	$SnCl_4.5H_2O$	Preparation of Stannic compound
14. Brimstone	Sulphur	S_8	In medicine
15. Carnallite	Hydrated Potassium and magnesium chloride	$KCl.MgCl_2.6H_2O$	Extr. *Mg*
16. Chile Saltpetre	Sodium nitrate	$NaNO_3$	HNO_3
17. Caustic Soda	Sodium hydroxide	$NaOH$	As solvent, prepn. of Na_2CO_3
18. Cuprite or Ruby Copper	Cuprous oxide	Cu_2O	In colouring glass
19. Celestine	Strontium Sulfate	$SrSO_4$	Extraction of *Sr*
20. Calamine	Zinc Carbonate	$ZnCO_3$	Extraction of *Zn*
21. Caustic Potash	Potassium hydroxide	KOH	(i) As solvent (ii) in the prepn. of K_2CO_3
22. Cadmiore		$CdS+BaSO_4$	As dye
23. Calomel	Mercurous Chloride	Hg_2Cl_2	(i) As electrode (ii) As purgative
24. Corrosive Sublimate	Mercuric Chloride	$HgCl_2$	In the sterilisation of instruments
25. Cinnabar (Makaradhwaja) (Rasa Sindur)	Mercuric Sulfide	HgS	(i) Extraction of *Hg* (ii) Medicine
26. Cerrusite	Lead carbonate	$PbCO_3$	White pigment
Cryollite	Sodium aluminium fluoride	Na_3AlF_6	As Flux

Common Name or Trade Name	*Chemical Name*	*Formula*	*Uses*
28. Chrome Alum	Hydrated potassium and chromium sulfate	$K_2SO_4.Cr_2(SO_4)_3.24H_2O$	In paint
29. Copper Glance	Cuprous sulfide	Cu_2S	In the extraction of *Cu*
30. Chrome yellow	Lead Chromate	$PbCrO_4$	As dye
31. Chalk, iceland spar, limestone, marble	Calcium Carbonate	$CaCO_3$	(i) In powder (ii) In Tooth Powder
32. Carborundum	Silicon Carbide	SiC	In cutting glasses
33. Dolomite	Equimolar mixture of calcium and magnesium carbonate	$CaCO_3+MgCO_3$	In the extraction of *Mg* and *Ca*
34. Dry Ice	Solid Carbon dioxide	CO_2 (solid)	As refrigerant
35. Epsom Salt	Magnesium Sulfate heptahydrate	$MgSO_4.7H_2O$	(i) As purgative (ii) In white cement
36. Fusion Mixture	Equimolar mixture of Sod. and Pot. Carbonate	$Na_2CO_3+K_2CO_3$	In salt test to decrease M.P.
37. Freon-12	Dichloro-difluoro methane	CF_2Cl_2	As refrigerant
38. Fulminating Gold	Gold-amide	 $Au\begin{matrix}\diagup NH\\ \diagdown NH_2\end{matrix}$	As explosive
39. Fool's Gold	Cadmium Sulfide *N.B.* In some books FeS_2	CdS	In colour
40. Franklinite	Zinc Ferric Oxide	$ZnO.Fe_2O_3$	Extraction of *Zn*
41. Felspar	Pot. aluminium silicate	$KAlSi_3O_8$	Mineral of *Al*
42. Ferric alum	Hydrated potassium and ferric sulfate	$K_2SO_4.Fe_2(SO_4)_3.24H_2O$	In germicide
43. Fenton Reagent	—	$FeSO_4+H_2O_2$	As reagent
44. Glauber Salt	Sodium sulfate decahydrate	$Na_2SO_4.10H_2O$	In the prepn. of $Na_2CO_3.10H_2O$
45. Gypsum	Calcium sulfate dihydrate	$CaSO_4.2H_2O$	(i) In Plaster of paris (ii) As hard materials
46. Graham's salt or Calgon	Sodium hexametaphosphate	$(NaPO_3)_6$ or $Na_2(Na_4P_6O_{18})$	In the removal of hardness of water
47. Green Vitriol	Ferrous sulfate heptahydrate	$FeSO_4.7H_2O$	(i) Green Ink (ii) As reagent
48. Galena	Lead Sulfide	PbS	(i) Extraction of lead (ii) In dye
49. Gun Powder	—	KNO_3+S + Charcoal	As explosive
50. Hypo	Sodium thiosulfate Pentahydrate	$Na_2S_2O_3.5H_2O$	(i) In photography (ii) As reagent
51. Horn Silver	Silver Chloride	$AgCl$	In the extraction of *Ag*
52. Hydrolith	Calcium hydride	CaH_2	In the prepn. of H_2
53. Heavy Water	Deuterium Oxide	D_2O	As moderator in nuclear reactor

Common or Trade Name	Chemical Name	Formula	Uses
54. Haematite	Ferric Oxide	Fe_2O_3	In the extraction of *Fe*
55. Lime Water	Solution of $Ca(OH)_2$	$Ca(OH)_2$	In the test of CO_2 and SO_2
56. Lithopone	—	$ZnS+BaSO_4$	As white paint
57. Lunar Caustic	Silver Nitrate	$AgNO_3$	(i) In the prepn. of $AgCl$ ii) In dye
58. Lead of Pencil	Graphite	C	In pencil
59. Lye	Sod. hydroxide solution	$NaOH$	As solvent
59a Lapis Lajuli	Sod. aluminium silicate	—	In ultramarine
60. Microcosmic Salt	Sod. amm. hydrogen phosphate tetrahydrate	$Na(NH_4)HPO_4.4H_2O$	In the test of silicate and prepn. of NH_3
61. Mosaic gold	Stannic sulfide	SnS_2	As paint
62. Magnesium alba	Basic magnesium carbonate trihydrate	$Mg(OH)_2.MgCO_3.3H_2O$	As anta-acid.
63. Milk of Lime	Calcium hydroxide	$Ca(OH)_2$	In mortar
64. Mohr's Salt	Ferrous ammonium sulfate	$FeSO_4(NH_4)_2SO_4.6H_2O$	As r.a. and per-/manganetometry
65. Mica	Pot. aluminium silicate	$K_2O.3Al_2O_3.6SiO_2.2H_2O$	Mineral of *Al*
66. Marsh Gas	Methane	CH_4	As illuminate
67. Rouge	Ferric Oxide	Fe_2O_3	In cleaning ornaments
68. Magnesia	Magnesium Oxide	MgO	In cement industry
69. Milk of magnesia	Magnesium hydroxide	$Mg(OH)_2$	In medicine
70. Nitrolim	Calcium Cyanamide	$CaCN_2$	In fertiliser
71. Nitre	Pot Nitrate	KNO_3	In explosive and in the prepn. of HNO_3
72. Nessler's Reagent	A solution of K_2HgI_4+KOH	—	Test for NH_3
73. Oleum	Fuming H_2SO_4	$H_2S_2O_7$	As very concentrated acid
74. Oil of Vitriol	Conc. H_2SO_4	H_2SO_4	As lab. reagent
75. Glass	Mixture of Sod. and Calcium Silicate	$Na_2SiO_3+CaSiO_3$	As glass
76. Phosgene gas	Carbonyl Chloride	$COCl_2$	As poisonous gas
77. Plaster of Paris	Semi-Hydrated Calcium sulfate	$CaSO_4.\frac{1}{2}H_2O$, $2CaSO_4.H_2O$, $(CaSO_4)_2H_2O$	By orthopaedic surgeon and in plastering walls
78. Producer gas	A mixture of $CO+N_2+H_2$	—	As fuel
79. Pearl ash	Pot Carbonate	K_2CO_3	In the prepn. of soap
80. Purple of Cassius	—	$AuCl_3+SnCl_2$	In electroplating
81. Philosopher's Wool	Zinc Oxide	ZnO	(i) As white paint (ii) in ointment
82. Quick lime	Calcium Oxide	CaO	(i) In fire bricks (ii) In the prepn. of slaked lime

Common or Trade Name	*Chemical Name*	*Formula*	*Uses*
83. Quick silver	Mercury	Hg	In thermometer
84. Quartz	Silica	SiO_2	In glass
85. Rochelle Salt	Sod. pot. tartarate	$CHOHCOONa$ | $CHOHCOOK$	In medicine
86. Red Lead	Red Oxide of Lead	Pb_3O_4	In paint
87. Sylvine	Pot. chloride	KCl	In the extraction of K
88. Schoenit	Hydrated Pot. magnesium sulfate	$K_2SO_4.MgSO_4.6H_2O$	Mineral of Mg
89. Shora	Potassium nitrate	KNO_3	In explosive
90. Salammoniac	Ammonium chloride	NH_4Cl	In the prepn. of NH_3
91. Sorel's Cement	—	$MgCl_2.5MgO.xH_2O$	In white cement
92. Superphosphate of lime	—	$Ca(H_2PO_4)_2.H_2O + 2(CaSO_4.2H_2O)$	As fertiliser
93. Strontianite	Strontium carbonate	$SrCO_3$	In the prepn. of Sr-salt
94. Silica gel	—	$SiO_2.xH_2O$	In the purification of water
95. Salt Cake	Sodium sulfate	Na_2SO_4	In $Na_2CO_3.10H_2O$
96. Tripasa	Sodium phosphate	$Na_3PO_4.12H_2O$	In fertiliser
97. Turquoise	—	$AlPO_4Al(OH)_3.H_2O$	In fertiliser
98. Washing Soda	Sod. carbonate	$Na_2CO_3.10H_2O$	(1) In washing (2) In the prepn. of soap
99. Water gas	$CO+H_2$	$CO+H_2$	As fuel
100. White Lead	Basic Lead carbonate	$2PbCO_3.Pb(OH)_2$	As white paint
101. White Vitriol	Zinc sulfate heptahydrate	$ZnSO_4.7H_2O$	In the prepn. of Zincite and calico-printing
102. Water glass	Sodium silicate	Na_2SiO_3	In glass
103. Witherite	Barium carbonate	$BaCO_3$	As poison
104. Willemite	Zinc silicate	Zn_2SiO_4	Mineral of Zn
105. Ultra marine	Sod. aluminium silicate	$Na_5Al_3Si_3SO_{12}$	As Blue dye
106. Vit eosil	Silicon dioxide	SiO_2	In glass
107. Zinc white	Zinc oxide	ZnO	As white and in Chinese ink
108. Zinc Blende	Zinc sulfide	ZnS	In the extraction of Zn

APPENDIX-4

Important Pigments in Inorganic Chemistry

Name of the Pigment	*Chemical Formula*
1. Chrome yellow	$PbCrO_4$
2. Zinc yellow	$Zn(OH)_2.ZnCrO_4.H_2O$
3. Chrome red	$PbCrO_4.PbO$
4. Red Lead	Pb_3O_4
5. Gulgret's green	$Cr_2O_3.2H_2O$
6. Prussian blue	$Fe_4[Fe(CN)_6]_3$
7. Sheele's green	$CuH.AsO_3$
8. Thenard's blue	$CoO.Al_2O_3$
9. Verdigris/Basic Copper acetate	$(CH_3COO)_2Cu\text{-}Cu(OH)_2$
10. Rinnman's Green	$ZnO.CoO$
11. White Zinc Oxide	ZnO
12. Lithopone	$ZnS+BaSO_4$
13. White Lead	$2PbCO_3.Pb(OH)_2$
14. White Basic Zinc Chromate	$ZnCrO_4.Zn(OH)_2$

APPENDIX-5

Important Reagents

Name of Reagent	*Test for*
1. Magnesia Mixture (a solution containing $MgCl_2$, NH_4Cl and NH_3)	Arsenate
2. Bettendorff's Test ($SnCl_2$ and conc. HCl)	Arsenious Compounds
3. Marsh's Test (Reduction of Arsenic by nascent Hydrogen in acid)	Arsenic Compounds
4. Dimethyl Glyoxime (DMG) Test (1 gm DMG in 100 cc rectified spirit)	Ni^{+2}

Name of Reagent	*Test for*
5. Chromyl Chloride Test (Chloride$+K_2Cr_2O_7+$Conc. H_2SO_4)	Cl^-
6. Fenton Reagent ($FeSO_4+H_2O_2$)	
7. Nessler's Reagent ($HgI_2+KI+NaOH$)	NH_3
8. Ring Test Nitrate$+FeSO_4$ (fresh, saturated soln.) $+$conc. H_2SO_4	NO_3^-
9. Lucas Reagent Conc. $HCl+$anhydrous $ZnCl_2$	1°, 2°, 3° alcohol
10. Tollen's Reagent (Ammoniacal $AgNO_3$)	$-CHO$
11. Fehling's Solution Fehling Solution 1→$CuSO_4$ Solution Fehling Solution 2→Rochelle's Salt $+NaOH$ soln.	$-CHO$
12. Schiff's Reagent (Solution of reduced form of p-rosaline hydrochloride)	$-CHO$

APPENDIX-6

Distinction Between Gases

Gases	*Distinguishing Reagent*	*Remarks*
1. CO_2 and SO_2	Acidified $K_2Cr_2O_7$ soln.	CO_2—no reaction SO_2—turns $K_2Cr_2O_7$ soln. green
2. NO and N_2O	Acidified $FeSO_4$ solution	NO—turns $FeSO_4$ soln. brown. N_2O—no reaction
3. N_2O and O_2	Alkaline Pyrogallol solution	O_2→is absorbed by alkaline Pyrogallol soln. N_2O→no reaction
4. NH_3 and HCl	(a) Litmus paper (b) Nessler's Reagent	(i) NH_3—turns red litmus blue (ii) HCl—turns blue litmus red (i) NH_3—turns Nessler's Reagent brown. (ii) HCl—no reaction
5. H_2 and O_2	Alkaline Pyrogallol solution	O_2 is absorbed; H_2 is not absorbed
6. SO_2 and H_2S	Lead acetate paper	H_2S—turns lead acetate paper black SO_2—no reaction
7. HCl and Cl_2	Starch iodide paper	Cl_2—turns moist starch iodide paper blue and bleached HCl—no reaction
8. HBr and HI	Conc. H_2SO_4	HBr—Brown Br_2-vapour is liberated HI—violet vapours of Iodine are formed
9. Cl_2 and Br_2(g)	Moist starch iodide paper	Cl_2—turns moist starch iodide paper blue and bleached Br_2—turns moist starch iodide paper blue
10. NH_3 and NO	Nessler's Reagent	NH_3—turns Nessler's Reagent brown NO—no reaction

Some Useful Constants

Constant	*Value in S.I. Units*	*Value in C.G.S. Units*
Avogadro's Number (N)	$6{\cdot}022 \times 10^{23}$ mole^{-1}	$6{\cdot}022 \times 10^{23}$ mole^{-1}
Planck's Constant (h)	$6{\cdot}626 \times 10^{-34}$ Js	$6{\cdot}626 \times 10^{-27}$ erg-sec.
Velocity of light (c)	$2{\cdot}997925 \times 10^{8}$ ms^{-1} $\approx 3 \times 10^{8}$ ms^{-1}	$2{\cdot}997925 \times 10^{10}$ cm-sec^{-1} $\approx 3 \times 10^{10}$ cm-sec^{-1}
Electron mass	$9{\cdot}1091 \times 10^{-31}$ kg	$9{\cdot}1091 \times 10^{-28}$ gm
Electronic charge (e)	$1{\cdot}60206 \times 10^{-19}$ coulomb	$9{\cdot}8022 \times 10^{-10}$e.s.u. $= 1{\cdot}60206 \times 10^{-19}$ coulomb
Proton mass	$1{\cdot}6725 \times 10^{-27}$ kg	$1{\cdot}6725 \times 10^{-24}$ gm
Neutron mass	$1{\cdot}6748 \times 10^{-27}$ kg	$1{\cdot}6743 \times 10^{-24}$ gm
Bohr radius	$5{\cdot}2918 \times 10^{-11}$ m	$5{\cdot}2918 \times 10^{-9}$ cm
Energy of the orbit	$-\frac{1313{\cdot}33}{n^2}$ kJ per mole	$-\frac{13{\cdot}6}{n^2}$ eV

Conversion Factors

$1\text{Å} = 10^{-8}$ cm $= 10^{-10}$ m

1 litre $= 1000$ c.c. $= 10^{-3}$ m^3; 1 atm. $= 101{,}325$ Nm^{-2}

1 Newton (N) $= 10^5$ dynes

1 cal $= 4{\cdot}184$ J $= 4{\cdot}184 \times 10^7$ ergs

1 erg $= 10^{-7}$ J

1 eV $= 1{\cdot}60206 \times 10^{-19}$ J $= 1{\cdot}60206 \times 10^{-12}$ erg $= 3{\cdot}83 \times 10^{-23}$ kcal

1 Joule $= 0{\cdot}2390$ cal

CHEMISTRY

CEE, Bihar, 1986

1. Write the chemical names and one use of the following :

(a) Bleaching powder (b) Phosphorite (c) Milk of magnesia (d) Vinegar (e) Marsh gas (f) Nichrome (g) Carbolic acid (h) Washing soda (i) Hypo (j) DDT.

2. Account for the following :

(i) The freezing point of water is lowered by the addition of common salt.

(ii) Phosphorus exists as red and yellow variety.

(iii) Solid iodine evaporates directly on heating.

(iv) Ammonia forms dense white fumes with HCl gas.

(v) Though nitric oxide is colourless it becomes brown on exposure to air.

3. State whether true or false :

(a) The chemical properties of an atom are determined by its nuclear charge.

(b) In an ordinary chemical reaction, the number of moles of the reactants always equals the number of moles of the product.

(c) One should expect that the heat produced in the reactions $H_2(g)+\frac{1}{2}O_2\rightarrow H_2O$ and $2C_2H_2+5O_2\rightarrow 2H_2O+4CO_2$, would have same numerical value.

(d) The average speed of a molecule depends on absolute-temperature.

(e) The greater the difference in the energy between two levels, the lower the wave length of light emitted, when an electron moves between them.

(f) Phenolphthalein can be used as an indicator in iodometry.

(g) The rate of reaction decreases with time.

(h) Exothermic reactions always become faster as we approach absolute zero.

(i) Dry ice is ultra dry water cooled to 20°C.

(j) Salt water can be purified by osmosis.

4. Give Balanced equations :

(i) $Cr_2O_7^{--}+Fe^{++}+H_3O^{+}\rightarrow Cr^{+++}+Fe^{+++}+H_2O$

(ii) $KClO_3\,(s)\rightarrow KClO_4+KCl$

(iii) A solution of lead nitrate is mixed with K_2CrO_4 solution.

(iv) A solution of sodium thiosulphate is treated with iodine in KI solution.

5. (a) Fill up the blanks to complete the nuclear reactions :

(i) ${}^{235}_{92}U+{}^{1}_{0}n\rightarrow(\quad)+\quad{}^{144}_{55}Cs+2\,{}^{1}_{0}n$

(ii) ${}^{214}_{82}Pb\rightarrow{}^{0}_{1}n+(\quad)$

(iii) ${}^{40}_{19}K+(\quad)\rightarrow{}^{37}_{17}Cl+\ {}^{4}_{2}He$

(b) (i) The half life of an isotope is 10 hrs. How much will be left behind after 4 hrs in 1 gm of the sample ?

(ii) A certain radioactive decay from ${}^{235}_{92}U$ ends up in ${}^{207}_{82}Pb$. In essence——α and ——β particles are emitted.

(iii) The half life of U^{238} to decompose to Pb^{206} is $4{\cdot}5\times10^{9}$ years. What will be the age of a rock that contains equal weights of both ?

6. (i) Write the electronic structure of acetaldehyde.

(ii) Draw the Lewis structure of Cl_2O.

(iii) $1s^2\ 2s^2\ 2p^6$ represents what element ?

Magadh University. I.Sc., 1987

Group A

1. Select the correct answer for the following :

(a) The nucleus of an atom consists of following particles :

(i) Neutron (ii) Proton

(iii) Electron and proton (iv) Proton and neutron

(b) Elements having same atomic number but different atomic weights are

(i) polymer (ii) isomer

(iii) isotope (iv) isobar

(c) The maximum covalency of sulphur is

(i) 2 (ii) 3 (iii) 4 (iv) 5 (v) 6

(d) The oxidation number of carbon in $C_6H_{12}O_6$ is

(i) 6 (ii) 4 (iii) -4 (iv) zero

(e) The number of electrons present in 1·6 gram of methane are

(i) $6{\cdot}023\times10^{23}$ (ii) $4\times6{\cdot}023\times10^{23}$

(iii) $10\times6{\cdot}023\times10^{23}$ (iv) 10

2. (a) Give a comparative account of the properties of alpha, beta and gamma rays.

(b) 500 ml of (N) $NaOH$ was mixed with 50 ml of (5N)HCl. The volume was made to 1000 ml. Find out the strength of the solution. Will it be acidic or basic ?

3. (a) What is Rutherford's model of atom ? Write down its drawbacks.

(b) How much sugar ($C_{12}H_{22}O_{11}$) will be required if each person on the earth is given 100 molecules of sugar ? The population of the earth is 3×10^{10}.

4. (a) What do you mean by equivalent weight of an oxidising agent ? Explain with example.

(b) Calculate the pH of 0·01 (N) $NaOH$ and M/2000 H_2SO_4.

(c) Write down the chief properties of covalent compounds.

Group B

5. (a) Describe any three methods of concentration of ores.

(b) Give an account of the chemical reactions taking place inside the blast furnace in manufacture of cast iron.

6. (a) How do metals differ from non-metals ?

(b) The first three elements of a group have the following electronic configurations :

$$A = 2, 2 \qquad B = 2, 8, 2 \qquad C = 2, 8, 8, 2$$

then (i) to what group the elements belong, (ii) what is the valency, and (iii) what are the periods of the elements ?

7. What are the principles involved in extraction of sodium from sodium chloride ?

How does sodium hydroxide react with phosphorus, carbon dioxide, chlorine and ammonium chloride ?

8. Describe the principle of extraction and purification of mercury from cinnabar.

How does mercury react with (a) S (b) Cl_2 (c) conc. H_2SO_4 and (d) dil. HNO_3 ?

9. Write down the principle of the manufacture of H_2SO_4 by any one method.

Show that the acid behaves as (a) an acid (b) a dehydrating agent and (c) an oxidising agent. Give examples.

10. How is iodine obtained from natural sources ? Write down a method of its manufacture.

How does iodine react with (a) H_2S (b) KI (c) Na_2SO_3 (d) P ?

11. (a) Describe the action of heat on the following :
(i) S (ii) green vitriol (iii) KNO_3 and (iv) NH_4Cl

(b) What tests are performed for detecting—
(i) nitrate (ii) nitrite (iii) sulphate (iv) sulphide ?

12. What happens when—

(a) $FeSO_4$ reacts with acidulated solution of $K_2Cr_2O_7$?
(b) PH_3 is passed through the solution of $CuSO_4$?
(c) Al is heated with solution of $NaOH$?
(d) $MgCl_2, 6H_2O$ is heated in air ?
(e) magnesium nitride is heated with water ?

Patna University, I. Sc., 1986

1. (a) The two electrons in a stable $2p^2$ configuration remain unpaired according to (i) Pauli's exclusion principle, (ii) Bohr's theory, (iii) Hund's rule, (iv) Aufbau principle.

(b) An electron in $3d$ orbital has the quantum numbers (i) $n=3$, $l=3$, (ii) $n=2$, $l=3$, (iii) $n=3$, $l=2$, (iv) $n=2$, $l=2$.

(c) An aqueous solution of HCl conducts electricity because (i) HCl is an electrovalent compound, (ii) H_2O is an electrovalent compound, (iii) both HCl and H_2O are electrovalent compounds, (iv) H_3O^+ and Cl^- are formed by the interaction of HCl and H_2O.

2. (a) Write down the electronic configurations of the elements having atomic numbers 19, 26 and 36.

(b) Elucidate the difference between covalent and coordinate linkages with the examples of H_2S and NH_4Cl.

3. Select and write the correct answer for the following :

(a) An element having electronic configuration $(Ar)\ 3d^24s^2$ is (i) s-block, (ii) p-block, (iii) d-block, (iv) f-block element.

(b) The second ionization potential of an element is (i) lower than, (ii) higher than, (iii) equal to the first ionization potential of the element.

(c) Diamond and graphite are (i) allotropes, (ii) isotopes, (iii) isobars, (iv) isomers of carbon.

(d) The main constituents of producer gas are (i) carbon monoxide and hydrogen, (ii) carbon monoxide and nitrogen, (iii) carbon monoxide and sulphur dioxide.

(e) Nessler's reagent is an alkaline solution of (i) $HgCl_2$, (ii) Hg_2Cl_2, (iii) $K_2(HgI_4)$, (iv) $Hg_2(NO_3)_2$.

4. (a) Explain the principles involved in the manufacture of sulphuric acid by contact process.

(b) Write down the electronic structures of H_2SO_3 and H_2SO_4.

5. How is chlorine manufactured by an electrolytic process ? How does it react with (a) ammonia and (b) sulphur dioxide, under different conditions ?

6. (a) Discuss the principles involved in the extraction of copper from copper pyrites. How is the metal refined ?

(b) How does copper sulphate react with ammonia solution ?

7. (a) Discuss the principles involved in the extraction of zinc from zinc blend. How is the metal purified ?

(b) How does zinc react with caustic soda solution ?

8. What happens when :

(a) Phosphorus reacts with hot concentrated sulphuric acid ?

(b) Stannous chloride solution is added to a solution of mercuric chloride ?

(c) Concentrated hydrochloric acid reacts with solid potassium permanganate ?

(d) Carbon dioxide is passed through brine saturated with ammonia ?

9. Explain :

(a) In what order the partial ionic character of the covalent bond will increase among HF H_2O and NH_3 ?

(b) In what order the atomic radius will increase among sodium, potassium and lithium ?

(c) Why halogens have the largest electron affinity;

(d) Why ionization potential increases with increasing atomic number in a period ?

10. Write short notes on the following :

(a) Electronegativity, (b) Selection of flux in metallurgy,
(c) Silver nitrate test for Cl^-, Br^-, and I^-,

Patna University, I Sc., 1987

Group A

1. As directed in each of the following, select answer from the given alternatives and write :

(a) A hypothetical radioactive atom X disintegrates in the manner given below, finally to X_3 :

$$X \xrightarrow{-\alpha} X_1 \xrightarrow{-\beta} X_2 \xrightarrow{-\beta} X_3$$

Then X_3 is —— of X and —— of X_1.

Choose the correct terms from the following to fill in the above two blanks :

(i) isotope, (ii) isobar, (iii) isotone, (iv) none.

(b) Total electrical charge of one mole of electron is equal to
(i) 1 e.s.u. (ii) 1 C, (iii) $1{\cdot}6 \times 10^{-19}$ C, (iv) 96500 C.

(c) 10 ml of 10% HCl (eq. wt. 36·5) were mixed with 10 ml of 10% $NaOH$ (eq. wt. 40) then the resulting solution would be
(i) acidic, (ii) alkaline, (iii) neutral.

(d) Which of the following elements has the lowest first ionisation potential ?

(i) Mg (12), (ii) Al (13), (iii) Si (14), (iv) Ca (20).

(e) pH of 0·5 M H_2SO_4 is

(i) 0, (ii) 0·301, (iii) 1, (iv) 5.

2. Describe in brief the experiment that led Rutherford to put forward his atomic model. What difficulties were there in adopting the model in toto ? How did Bohr overcome those difficulties ?

3. (a) Write down electronic configuration of Cu (29) and Se (34), and tell on this basis the blocks of elements to which they belong.

(b) Calculate oxidation number of underlined atoms in the following : $\underline{Mn}O_4^{-2}$, $\underline{N}H_4\underline{N}O_3$.

(c) An element consists of two isotopes, one with mass 39·0 amu is 93% and the other with mass 41·0 amu is 7%. What is the atomic weight of the element ?

4. (a) Compare alpha, beta and gamma rays in respect of their nature, penetrating power and ionising power.

(b) $\frac{7}{8}$ of original polonium-210 decays to a stable isotope of lead in 420 days, calculate half life of polonium-210 isotope.

(c) Why can silver nitrate solution not precipitate silver chloride from carbon tetrachloride where it does with sodium chloride ?

Group B

5. Select the correct answer from the given alternatives in each of the following :

(a) Which of the following would decrease from left to right across a period in the periodic table ?

(i) Ionisation potential, (ii) Electronegativity, (iii) Atomic radii, (iv) Non-metallic character.

(b) Which group of elements would belong to *f*-block ?

(i) Alkaline earths, (ii) Rare earths, (iii) Rare gases, (iv) Alkali metals.

(c) Which of the pairs of elements has diagonal relationship ?

(i) Li, Mg, (ii) P, O, (iii) Al, Si, (iv) S, Br.

(d) Which of the following hydroxide is amphoteric ?

(i) NH_4OH, (ii) $Ca(OH)_2$, (iii) $Zn(OH)_2$, (iv) $Cu(OH)_2$.

(e) Which would be a suitable drying agent for ammonia gas ?

(i) H_2SO_4, (ii) P_2O_5, (iii) CaO, (iv) $CaCl_2$.

(f) To which kind of ore the froth flotation method of concentration is most applicable ?

(i) Chloride, (ii) Oxide, (iii) Sulphide, (iv) Sulphate.

(g) Whose aqueous solution of the following will precipitate a normal carbonate on addition of ammonium carbonate solution ?

(i) $NaCl$, (ii) $MgCl_2$, (iii) $CaCl_2$, (iv) $CuCl_2$.

(h) Which of the following is a dibasic acid ?

(i) HPO_3, (ii) H_3PO_2 (iii) H_3PO_3, (iv) H_3PO_4.

6. Discuss the principle of extraction of pure aluminium from bauxite. What is alumino-thermic process ?

7. (a) Discuss briefly the principle involved in any two of the following :

(i) Haber process of manufacture of ammonia,

(ii) Solvey's process of manufacture of sodium carbonate,

(iii) Ostwald's process of manufacture of nitric acid.

(b) How will you convert any nitrate into ammonia ?

8. Give reasons for the following using equations where necessary :

(a) Why can hydroiodic acid be not prepared by action of conc. H_2SO_4 on iodide ?

(b) Why can anhydrous magnesium chloride be not prepared by heating hydrated salt ?

(c) What makes phosphine prepared in the laboratory burn spontaneously in air ?

(d) Why can $CuSO_4$ be not separated from ferrous sulphate by fractional crystallisation ?

(e) Why is it difficult to isolate sodium by electrolysis of pure molten $NaCl$?

9. How will you demonstrate the presence of :

(a) Nitrogen in nitric acid, (b) Hydrogen in ammonia,

(c) Sulphur in SO_2, (d) O_2 in $Ca(OCl)Cl$?

10. Describe the reactions taking place in blast furnace during manufacture of cast-iron from iron ores.

How are ferrous and ferric salts distinguished ?

11. (a) Write down the bond structure of any *three* of the following showing lone pair of electrons, if any, by dots :

(i) O_3, (ii) SO_2, (iii) NO_3^-, (iv) PCl_3, (v) P_4O_{10}.

(b) Describe production and uses of any *one* of the following :

(i) Plaster of Paris (ii) Calomel.

12. What happens when :

(a) hydrogen sulphide is passed through an acidified solution of $K_2Cr_2O_7$?

(b) copper sulphate solution is treated with hydroiodic acid ?

(c) white phosphorus is boiled with caustic soda solution ?

(d) nitric oxide gas is passed through acidified $KMnO_4$?

Roorkee 1986

1. (a) The ionization energy of hydrogen atom is 13·6 eV. What will be the ionization energy of He^+ and Li^{+2} ions ?

(b) Write the electronic configurations of Cr^{+2} and Mn^{+4} and give the number of unpaired electrons present in each case.

(c) Balance the following equation by the oxidation state method :

$$Cr_2O_7^{-2}+I^-+H^+\rightarrow Cr^{+3}+I_2+H_2O$$

2. Give proper reasoning for the following :

(i) BF_3 molecular is non-polar.

(ii) Water is, generally, a good solvent for ionic compounds.

(iii) The electron affinity of nitrogen is lower than that of carbon.

3. (a) Arrange the following with proper explanations :

(i) Li, Na, K, Rb, and Cs in the increasing order of their hydrated ionic radii.

(ii) C, Si, Sn and Pb in the increasing order of stability of their $+2$ oxidation state.

(iii) $NaCl$, $MgCl_2$ and $AlCl_3$ in the increasing order of their covalent character.

(b) Write action of strong heat on the following :

(i) $AgNO_3$,

(ii) $Na_2B_4O_7.10H_2O$ (Give chemical equations also).

(c) Identify (A), (B), (C) and (D) and give their chemical formulae :

(i) $(A)+NaOH\xrightarrow{\text{heat}}NaCl+NH_3+H_2O$.

(ii) $NH_3+CO_2+H_2O\longrightarrow(B)$.

(iii) $(B)+NaCl\longrightarrow(C)+NH_4Cl$.

(iv) $(C)\xrightarrow{\text{heat}}Na_2CO_3+H_2O+(D)$.

4. Give proper reasoning for the following :

(i) Alkali metal salts impart colour to the flame.

(ii) Anhydrous $AlCl_3$ fumes in humid air.

(iii) H_2S acts only as a reducing agent while SO_2 can act both as a reducing and oxidizing agent.

(iv) An acidified $K_2Cr_2O_7$ paper on being exposed to SO_2 turns green.

(v) $HgCl_2$ and $SnCl_2$ cannot exist as such if present together in an aqueous solution.

Give eq^n. for (iv) and (v).

5. (a) An unknown inorganic compound (X) loses its water of crystallization on heating and its aqueous solution gives the following reactions :

(i) It gives a white turbidity with dilute HCl solution.

(ii) It decolourises a solution of iodine in KI.

(iii) It gives a white precipitate with $AgNO_3$ solution which turns black on standing.

Identify the compound (X) and give chemical equations for the reactions at step (i), (ii) and (iii).

(b) A certain inorganic compound (A) on heating loses its water of crystallization. On further heating a blackish brown powder (B) and two oxides of sulphur (C and D) are obtained. The powder (B) on boiling with HCl gives a yellow solution (E). When H_2S is passed in (E) a white turbidity (F) and an apple green solution (G) are obtained.

The solution (E) on treatment with this cyanate ions gives a blood red coloured compound (H). Identify from (A) to (H).

(c) What is meant by roasting of an ore ? Give one example with relevant equations.

Roorkee 1987

1. (a) Calculate the velocity (cm/sec) of an electron placed in the third orbit of the hydrogen atom. Also calculate the number of revolution per second that this electron makes around the nucleus.

(b) Arrange the electrons represented by the following sets of quantum numbers in the decreasing order of energy.

(i) $n=4,\ l=0,\ m_l=0,\ m_s=+\frac{1}{2}$

(ii) $n=3,\ l=1,\ m_l=1,\ m_s=-\frac{1}{2}$

(iii) $n=3,\ l=2,\ m_l=0,\ m_s=+\frac{1}{2}$

(iv) $n=3,\ l=0,\ m_l=0,\ m_s=-\frac{1}{2}$

(c) Which of the following compounds has the largest dipole moment :

(i) CH_3OH, (ii) CH_4, (iii) CF_4, (iv) CO_2 and, (v) CH_3F? Support your answer with proper reasoning.

2. Explain with proper reasoning :

(i) The formation of F^-(g) from F(g) is exothermic whereas that of O^{2-}(g) from O(g) is endothermic.

(ii) The three carbon-oxygen bonds are equal in the carbonate ions.

3. (a) Arrange the following with proper explanations.

(i) $LiCl$, $LiBr$ and LiI in the decreasing order of their covalent character.

(ii) N, P, As, Sb and Bi in the increasing order of stability of $+5$ oxidation state.

(iii) HF, HCl, HBr and HI in the increasing order of their acid strength.

(b) From the reactions given below, identify (A), (B), (C) and (D), and give their formulae :

(i) $(A) + \text{dil } H_2SO_4 + K_2Cr_2O_7 \longrightarrow (B)$ green coloured

$(A) + \text{dil } H_2SO_4 + (C) \longrightarrow MnSO_4$

$(A) + O_2 \xrightarrow{H_2O} (D)$

(ii) $(A)\ \text{aq} + Zn \xrightarrow{\text{heat}} (B)$ gas

$(A)\ \text{aq} + (C) \xrightarrow{\text{heat}} PH_3$

$(A)\ \text{aq} + NH_4Cl \xrightarrow{\text{heat}} (D)$ gas.

4. Explain the following with proper reasoning :

(i) Fe^{+3} is more stable than Fe^{+2}.

(ii) HNO_3 acts only as an oxidising agent while HNO_2 can act both as an oxidising and reducing agent.

(iii) Alkaline earth metal salt are diamagnetic.

(iv) Fluorine is a better oxdising agent than chlorine.

(v) H_2O_2 is used for restoring old painting in the museums.

5. (a) Using HNO_3 how will you obtain the following in one step :

(i) Hydrogen, (ii) Phosphoric acid ?

Stating the conditions of the reaction give balanced chemical equations.

(b) A black coloured compound (A) on reaction with dilute H_2SO_4 gives a gas (B) which on passing in a solution of an acid (C) gives a white turbidity (D). Gas (B) when passed in an acidified solution of a compound (E) gives a precipitate (F) soluble in dilute HNO_3. After boiling this solution when an excess of NH_4OH is added a blue coloured compound (G) is formed. To this solution on addition of acetic acid and aqueous $K_4[Fe(CN)_6]$ a chocolate precipitate (H) is obtained. On addition of an aqueous solution of $BaCl_2$ to an aqueous solution of (E) a white precipitate insoluble in HNO_3 is obtained. Identify from (A) to (H).

(c) Which of the following metals can be obtained by the electrolytic reduction of aqueous solution of their salts :

Al, *Na*, *Cu* and *Ag* ?

Support your answer with proper reasoning.

B. I. T., Mesra, 1986

1. Explain the following statements :

(a) Hydrogen sulphide (H_2S) is a gas at room temperature, while water (H_2O) is a liquid at room temperature, though water is having less molecular weight than H_2S.

(b) Pure zinc is only attacked very slowly by dilute acids and it is customary to add a little copper sulphate solution to the acid to obtain a steady evolution of hydrogen.

(c) Marsh gas detector, used by miners, is a practical application of the phenomenon of diffusion and it functions on the principle of Graham's Law of Diffusion.

(d) A sample of very pure sodium chloride can be obtained by passing pure and dry HCl gas through a strong solution of brine.

2. Complete the following equations and finally balance each one of the following equations :

(a) $NH_3+Cl_2\rightarrow\ldots\ldots\ldots+NH_4Cl$

(b) $HgCl_2+H_3PO_3+H_2O\rightarrow\ldots\ldots\ldots+HCl+H_3PO_4$

(c) $Na_2S_2O_3+HCl\rightarrow NaCl+\ldots\ldots\ldots+\ldots\ldots+H_2O$

(d) $NaIO_3+NaHSO_3\rightarrow\ldots\ldots\ldots+NaHSO_4+\ldots\ldots+H_2O$

(e) $Sn+HNO_3$ (conc.)$\rightarrow\ldots\ldots+NO_2+H_2O$

3. Fill in the blank spaces in each case with the *most appropriate* word or words so that the completed statements should give the expected chemical meaning :

(a) Aqua regia is a mixture of......parts of......and part (s) of......and is useful in dissolving......metals.

(b) Hydrogenation of oils is carried out by passing hydrogen through the oil in the presence of finely divided......and this is the principle on which 'Dalda' (solid fat) is manufactured.

(c) The principle involved in the bleaching property of SO_2 is due to......of coloring matter to a colorless product (e.g. a moist colored flower gets decolorized by SO_2 gas).

(d) Certain metals such as sodium or zinc react with mercury to furnish alloys which are generally termed as......

(e) Fuming nitric acid fails to dissolve iron as it forms a layer of......and is generally termed as......of iron.

4. (a) Choose *the wrong* statement among the following list and rewrite it in *the correct form* :

(i) Hydrated magnesium sulphate is used as a purgative.

(ii) Anhydrous zinc chloride is obtained by heating hydrated zinc chloride ($ZnCl_2.2H_2O$).

(iii) Chloroform can be prepared easily by the action of chlorine and alkali ($NaOH$) on methyl alcohol.

(b) Indicate which one among the following list (i to iv) represents accurately the composition of the German silver :

(i) $Cu(50\%); Zn(5\%); Ni(45\%)$
(ii) $Cu(10\%); Zn(65\%); Ni(25\%)$
(iii) $Cu(10\%); Zn(80\%); Ni(10\%)$
(iv) $Cu(50\%); Zn(25\%); Ni(25\%)$.

(c) Describe a good *laboratory chemical* test to distinguish between the following pairs of compounds :

(i) Acetaldehyde and Diethyl ether

(ii) Ferrous ammonium sulphate (Mohr's salt) in solution and ferric ammonium sulphate in solution.

(iii) Nitric oxide (colourless gas) from Nitrous oxide (colourless gas).

(d) Explain *in two sentences* the following observations :

(i) The salt solution has to be boiled with a drop of nitric acid before proceeding with group-III analysis.

(ii) NH_4Cl is *also* needed along *with* excess of NH_4OH to precipitate group-III metals.

(e) Describe the reagent considered to be highly efficient to detect ammonia (even in traces) in a given sample of the solution. (Avoid tests involving $NaOH$ or HCl)

5. (a) What do you understand by the statement 'Golden-spangles Test' and where do you encounter it ?

(b) How do you prove experimentally that diamond and graphite are allotropic modifications of the element "*carbon*" ?

Indian School of Mines (ISM), 1986

1. (a) Name two important ores of copper and give their formulae. Give the names of two important alloys of copper.

(b) Give equations for the chemical reactions in the process of bessemerisation in the extraction of *Cu*.

(c) Give the reactions taking place in the blast furnace in the smelting of iron.

(d) Describe the method for the preparation of 99·99% pure *Al* from moderately pure *Al*.

2. (a) What is the difference between ortho-hydrogen and para-hydrogen ?

(b) Define half-life period. At a certain instant a piece of radioactive material contains 10^{12} atoms. The half-life of the material is 30 days. Calculate the number of disintegrations in the first second.

3. (a) Discuss sigma and pi bond giving examples of methane and benzene.

(b) Give the resonance hybrid structure of H_3PO_3.

Indian School of Mines (ISM), 1987

PART A

1. (a) Why is the sintering step necessary in the metallurgy of iron ?

(b) What is cast iron ? Why is it called *cast* iron ? Why is it not suitable for forging ?

(c) What is wrought iron ? Why is it particularly suitable for making electro-magnets ?

(d) What is steel ? How does carbon content improves the quality of steel ? How is hardening of steel done ?

2. Explain—

(a) Why CuS is precipitated by passing H_2S in an acidic medium, but NiS is not ?

(b) Why does $Al(OH)_3$ dissolve in $NaOH$ solution, but $Cr(OH)_3$ does not ?

(c) Why is the filtrate from analytical Gr II, boiled free of dissolved H_2S and then it is to be boiled with a few drops of conc. HNO_3 before adding the group reagents, NH_4Cl and NH_4OH ?

(d) Why does $AgCl$ dissolves in NH_4OH ?

PART B

3. What do you understand by the terms

(a) orbits, (b) suborbits, and

(c) orbital ?

4. Sub-atomic particle transitions in an atom result in the emission of electromagnetic radiation.

Match the types of transition given in Column I below with the types of radiation given in Column II—

I	II
(a) Electron transition from outer atomic orbits.	(a) X-rays
(b) Filling up the electron vacancy in an inner atomic orbit by an electron from an outer atomic orbit.	(b) Gamma rays

I	II
(c) Sub-nuclear particles transition in an atomic nucleus.	(c) Ultra-violet, visible and infra-red radiations.

In what energy range (electron volts, kilo-electron volts, million electron volts) the radiations under II (a), (b) and (c) will be ?

5. (i) In the reactions—

(a) $2KI + Cl_2 = 2KCl + I_2$

(b) $2KClO_3 + I_2 = 2KIO_3 + Cl_2$

why does Cl replace I in (a) while I replaces Cl in (b) ?

(ii) In the reactions—

(a) $SnCl_2 + 2FeCl_3 = SnCl_4 + 2FeCl_2$

(b) $PbCl_4 \xrightarrow{\text{Heat}} PbCl_2 + Cl_2$

reaction (a) shows that *Sn* (IV) is more stable than *Sn* (II) and reaction (b) shows that *Pb* (II) is more stable than *Pb* (IV). Both *Sn* and *Pb* belong to Group IV of the periodic table and *Pb* has a higher atomic number than *Sn*. Can you explain the reactions ?

6. What do you understand by the terms

(i) mass defect, and

(ii) nuclear binding energy ?

Calculate the mass defect and binding energy per nucleon for an alpha-particle (containing two protons and two neutrons) whose actual mass is 4·0028 a.m.u.

I. I. T., 1986

PART 'A'

1. For each sub-question given below four answers are provided of which only ONE is correct. Write down the *correct answer* on the answerscript as illustrated by the following example :

[The *pH* of pure water at 25°C is close to

(A) 2 (B) 7 (C) 10 (D) 12

The answer is to be given as (B)]

(i) Rutherford's alpha particle scattering experiment eventually led to the conclusion that—

(A) mass and energy are related

(B) electrons occupy space around the nucleus

(C) neutrons are buried deep in the nucleus

(D) the point of impact with matter can be precisely determined.

(ii) The bond between two identical non-metal atoms has a pair of electrons—

(A) unequally shared between the two

(B) transferred fully from one atom to another
(C) with identical spins
(D) equally shared between them.

(iii) Which one of the following sets of quantum numbers represents as impossible arrangement ?

	n	l	m_l	m_s
(A)	3	2	-2	1/2
(B)	4	0	0	1/2
(C)	3	2	-3	1/2
(D)	5	3	0	$-1/2$

(iv) The compound insoluble in acetic acid is—
(A) calcium oxide
(B) calcium carbonate
(C) calcium oxalate
(D) calcium hydroxide.

(v) The pair of compounds which cannot exist together in solution is—
(A) $NaHCO_3$ and $NaOH$
(B) Na_2CO_3 and $NaHCO_3$
(C) Na_2CO_3 and $NaOH$
(D) $NaHCO_3$ and $NaCl$.

(vi) The compound whose 0·1 M solution is basic is—
(A) ammonium acetate
(B) ammonium chloride
(C) ammonium sulphate
(D) sodium acetate.

(vii) Which one among the following pairs of ions cannot be separated by H_2S in dilute hydrochloric acid ?
(A) Bi^{3+}, Sn^{4+}
(B) Al^{3+}, Hg^{2+}
(C) Zn^{2+}, Cu^{2+}
(D) Ni^{2+}, Cu^{2+}

(viii) The compound which gives off oxygen on moderate heating is—
(A) cupric oxide
(B) mercuric oxide
(C) zinc oxide
(D) aluminium oxide

(ix) The hydrogen bond is strongest in—
(A) $O—H\ldots\ldots S$
(B) $S—H\ldots\ldots O$
(C) $F—H\ldots\ldots F$
(D) $F—H\ldots\ldots O$

(x) The hybridisation of sulphur in sulphur dioxide is—
(A) sp
(B) sp^3
(C) sp^2
(D) dsp^2

(xi) The bonds present in N_2O_5 are—
(A) only ionic
(B) covalent and coordinate
(C) only covalent
(D) covalent and ionic

2. (a) Amongst the four alternate answers are given for the sub-questions below, *one* or *more* are correct. Write down *all* the correct answers.

[Example : Solid sodium chloride is (A) ionic (B) brittle (C) non-conductor (D) covalent. Correct answers : (A, B, C).]

(i) Dipole moment is shown by—
(A) 1,4-dichlorobenzene
(B) cis 1,2-dichloroethene
(C) trans 1,2-dichloroethene
(D) trans 1,2-dichloro-2-pentene

(ii) CO_2 is isostructural with—

(A) $HgCl_2$ (B) $SnCl_2$

(C) C_2H_2 (D) NO_2

(iii) The sum of the number of neutrons and proton in the isotope of hydrogen is—

(A) 6 (B) 5 (C) 4 (D) 3

(iv) In the electrolysis of alumina, cryolyte is added to—

(A) lower the melting point of alumina

(B) increase the electrical conductivity

(C) minimise the anode effect

(D) remove impurities from alumina

3. (a) State if the following statements are *TRUE* or *FALSE*—

(i) The softness of group IA metals increases down the group with increasing atomic number.

(ii) The electron density in the XY plane in $3d_{x^2-y^2}$ orbital is zero.

(b) Give reasons in *ONE* or *TWO* sentences for each of the following—

(i) Hydrogen peroxide is a better oxidising agent than water.

(ii) Most transition metal compounds are coloured.

4. (a) Arrange the following in the order of their

(i) increasing size :

Cl^-, S^{2-}, Ca^{2+}, Ar

(ii) increasing acid strength :

$HClO_3$, $HClO_4$, $HClO_2$, $HClO$

(iii) increasing bond strength :

HCl, HBr, HF, HI

(iv) increasing oxidation number of iodine :

I_2, HI, HIO_4, ICl

(b) Match the following choosing one item from column X and the appropriate item from column Y.

X	Y
Lewis acid	K-electron capture
Philospher's wool	Zinc ore
Electrophile	$HCHO$
Preservative	NH_4^+
Electron emission	Small proton to neutron ratio
Bronsted acid	SO_3
Black Jack	BF_3
X-ray emission	ZnO

PART 'B'

5. (a) Complete and balance the following reactions :—

(i) $Mn^{2+}+PbO_2 \longrightarrow MnO_4^-+H_2O$
(ii) $S+OH^- \longrightarrow S^{2-}+S_2O_3^{2-}$
(iii) $ClO_3^-+I^-+H_2SO_4 \longrightarrow Cl^-+HSO_4^-$
(iv) $Ag^++AsH_3 \longrightarrow H_3AsO_3+H^+$

5. (b) Write the Lewis dot structure of the following :—

O_3, $COCl_2$.

5. (c) Mention the products formed in the following :—

(i) Chlorine gas is bubbled through a solution of ferrous bromide.

(ii) Zinc oxide is treated with excess of sodium hydroxide solution.

(iii) Iodine is added to a solution of stannous chloride.

(iv) Sulphur dioxide gas, water vapour and air are passed over heated sodium chloride.

6. $^{234}Th_{90}$ disintegrates to give $^{206}Pb_{82}$ as the final product. How many α and β particles are emitted during this process ?

I. I. T., 1987

PART 'A'

1. For each sub-question given below, four answers are given of which only *one* is correct. Write down the *correct answer* in the answerbook as illustrated by the following example :—

[The lightning bolts in the atmosphere cause the formation of :—
(A) NO (B) NH_3 (C) NH_4OH (D) NH_2OH.

The answer is to be given as (A).]

(i) The first ionisation potentials in electron volts of nitrogen and oxygen atoms are respectively given by—

(A) 14·6, 13·6, (B) 13·6, 14·6, (C) 13·6, 13·6, (D) 14·6, 14·6.

(ii) Atomic radii of fluorine and neon in Ångstrom units are respectively given by—

(A) 0·72, 1·60, (B) 1·60, 1·60,
(C) 0·72, 0·72, (D) None of these values.

(iii) The brown ring complex compouud is formulated as $[Fe(H_2O)_5(NO)^+]SO_4$. The oxidation state of iron is—

(A) 1, (B) 2, (C) 3, (D) 0.

(iv) The electronegativity of the following elements increases in the order—

(A) C, N, Si, P, (B) N, Si, C, P,
(C) Si, P, C, N, (D) P, Si, N, C.

(v) Of the following compounds, which will have a zero dipole moment ?

(A) 1, 1-dichloroethylene, (B) *cis*-1, 2 dichloroethylene,
(C) *trans*-1, 2 dichloroethylene, (D) None of these compounds.

(vi) Which of the following oxides of nitrogen is a coloured gas ?

(A) N_2O, (B) NO, (C) N_2O_4, (D) NO_2.

(vii) The metallic lustre exhibited by sodium is explained by—

(A) diffusion of sodium ions,
(B) oscillations of loose electrons,
(C) excitation of free protons,
(D) existence of body centred cubic lattice.

(viii) Amongst the trihalides of nitrogen, which one is least basic ?

(A) NF_3, (B) NCl_3, (C) NBr_3, (D) NI_3.

(ix) Hydrogen bonding is maximum in—

(A) Ethanol, (B) Diethyl ether
(C) Ethyl chloride, (D) Triethyl amine.

(x) Bromine can be liberated from potassium bromide solution by action of—

(A) Iodine solution, (B) Chlorine water,
(C) Sodium chloride, (D) Potassium iodide.

2. Fill in the blanks with appropriate words—

(i) Hydrogen gas is liberated by the action of aluminium with concentrated solution of ....

(ii) Silver chloride is sparingly soluble in water because its lattice energy is greater than..........energy.

(iii) ....phosphorus is reactive because of its highly strained tetrahedral structure.

3. State whether the following statements are *TRUE* or *FALSE*. If *FALSE*, give the correct statement.

(i) In benzene, carbon uses all the three p-orbitals for hybridisation.

(ii) Sodium when burnt in excess of oxygen gives sodium oxide.

(iii) Catalyst makes a reaction more exothermic.

(iv) Graphite is a better lubricant on the moon than on the earth.

(v) sp^2 hybrid orbitals have equal s and p character.

(vi) From the solution containing copper (+2) and zinc (+2) ions, copper can be selectively precipitated using sodium sulphide.

(vii) In Group IA, of alkali metals, the ionisation potential decreases down the group. Therefore, lithium is a poor reducing agent.

4. Write balanced equations for the following reactions :—

(i) Phosphorus is reacted with boiling aqueous solution of sodium hydroxide in an inert atmosphere.

(ii) Dilute nitric acid is slowly reacted with metallic tin.

(iii) Potassium permanganate is reacted with warm solution of oxalic acid in the presence of sulphuric acid.

(iv) Gold is dissolved in *aqua regia.*

(v) Acetamide is reacted with bromine in the presence of potassium hydroxide.

5. (a) Explain the following in *one* or *two* sentences only :—

(i) Magnesium oxide is used for the lining of steel making furnace.

(ii) The mixture of hydrazine and hydrogen peroxide with a copper (II) catalyst is used as a rocket propellant.

(iii) Orthophosphorous acid is not tribasic acid.

(iv) The molecule of magnesium chloride is linear whereas that of stannous chloride is angular.

(b) A mixture of two salts was treated as follows :—

(i) The mixture was heated with manganese dioxide and concentrated sulphuric acid, when yellowish green gas was liberated.

(ii) The mixture on heating with sodium hydroxide solution gave a gas which turned red litmus blue.

(iii) Its solution in water gave blue precipitate with potassium ferricyanide and red coloration with ammonium thiocyanate.

(iv) The mixture was boiled with potassium hydroxide and the liberated gas was bubbled through an alkaline solution of K_2HgI_4 to give brown precipitate.

Identify the two salts. Give ionic equations for reactions involved in the tests (i), (ii) and (iii).

PART 'B'

6. (a) Answer the following questions briefly :—

(i) What is the actual reducing agent of haematite in blast furnace ?

(ii) Give the equations for the recovery of lead from Galena by air reduction.

(iii) Why is sodium chloride added during electrolysis of fused anhydrous magnesium chloride ?

(iv) Zinc and not copper is used for the recovery of metallic silver from complex $[Ag(CN)_2]^-$. Explain.

(v) Why is chalcocite roasted and not calcinated during recovery of copper ?

□□□

ANSWERS

CHAPTER I Structure of Atom (Pages 51-58)

48. (a) Aluminium; (b) Phosphorus; (c) Copper. **49**. (a) 13; (b) 6; (c) 13; (d) 3; (e) Aluminium. **50**. (a) protons, electrons and neutrons, (b) protons; neutrons; electrons, protons, neutrons.

(c) oxygen. (d) neutrons.

51. $12 \rightarrow 6, 6, 6, +6$
$13 \rightarrow 6, 6; 7; 6, +6$.

52. (i) $2n^2$, (ii) 3, (iii) $n=2$; $l=1$, (iv) 0, 1, 2, (v) 2, 4.

53. **True** :—(iii), (iv), (v), (vii), (ix), (x).
False :—(i), (ii), (vi), (viii).

54. 1. —(e). 2. —(f) 3. —(b) 4. —(a)
5. —(g) . 6. ..(c). 7. —(h). 8. —(d).

55. 1. (c), 2. (a), 3. (b), 4. (e),
5. (e), 6. (d), **58**. 0, 1.

59. (a) $n=3, l=0$, (b) $n=2, l=1$, (c) $n=3, l=2$.

Numericals

76. $3{\cdot}30 \times 10^{-19}$ J and $4{\cdot}95 \times 10^{-19}$ J.

Comparing $\dfrac{4{\cdot}95 \times 10^{-19}\text{ J}}{3{\cdot}30 \times 10^{-19}\text{ J}} = 1{\cdot}5$.

77. (a) $6{\cdot}023 \times 10^{23}$ electron,

(b) C_2H_6 (Mol wt $=30$) no. of $\bar{e} = 2C + 6H = 2 \times 6 + 6 \times 1 = 18$

$= 18 \times 6{\cdot}023 \times 10^{23}\bar{e}$.

78. Mol wt $=92$. The oxide is N_2O_4.
Total no. of electrons $= 2N + 4(O) = 2 \times 7 + 4 \times 8 = 14 + 32 = 46 \times N$.

79. Using $E_2 - E_1 = hcR\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$

$$=6{\cdot}627\times10^{-27}\times3\times10^{10}\times109737\left(\frac{1}{1^2}-\frac{1}{2^2}\right)$$

$$=1{\cdot}635\times10^{-11}\text{ ergs.}$$

81. E_2-E_1 (emission) $=hcR\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$

$$=6{\cdot}627\times10^{-27}\times3\times10^{10}\times109737\left(\frac{1}{3^2}-\frac{1}{5^2}\right)\text{ ergs.}$$

82. $\triangle x.\triangle p=\frac{h}{2\pi}$

or $\triangle x=\frac{h}{2\pi}\times\frac{1}{\triangle p}=\frac{6{\cdot}627\times10^{-27}}{2\times\frac{22}{7}}\times1\times10^{-4}=1{\cdot}05\times10^{-31}$ cm.

83. 7266Å $\left(\text{By } \lambda=\frac{h}{mv}\right)$.

84. 10^{-10} m. $\left(\text{By } \triangle p\triangle x=\frac{h}{4\pi}vm\triangle v\triangle x=\frac{h}{4\pi}\right)$,

85. (a) $6{\cdot}6\times10^{-24}$ kg ms^{-1} $\left(\text{By } \lambda=\frac{h}{p}=\frac{h}{mv}\right)$.

(b) $3{\cdot}732\times10^{-36}$ kg $\left(\text{By } m=\frac{h}{\lambda v}\right)$.

86. d. **87.** a. **88.** d. **89.** c. **90.** c. **91.** b.
92. d. **93.** a. **94.** d. **95.** b wrongly written 'c'.
96. a. **97.** b. **98.** b. **99.** d. **100.** c. **101.** d.
102. c. **103.** a. **104.** d. **105.** a. **106** b.

CHAPTER 2 Radioactivity (Pages 88-94)

12. (a). 1. (j). 2. (g). 3. (i). 4. (c).
5. (k). 6. (b). 7. (l). 8. (a). 9. (f).
10. (e). 11. (d). 12. (h). 13. (n). 14. (m).

12. (b)—

(a) $-\frac{dN}{dt}$.

(b) effective

(c) β particle (β^-)

(d) positron ($_{+1}^{0}e$ or β^+)

(e) $^{14}_{6}C$ no. of neutrons $=14-6=8$ ($^{14}_{6}C\rightarrow{}^{14}_{7}N+{}^{0}_{-1}e$)

13. $7{\cdot}1\times10^{-26}$ gm.

14. $2{\cdot}31 \times 10^{10}$ d.p.s.
15. 5·52 hours.
16. 1·52 hours.
17. 0·076%.

18. $\lambda = 0{\cdot}02772$ day^{-1}; $t_{\frac{1}{2}} = 25$ days; $T = \frac{1}{\lambda} = 36{\cdot}075$ days.

19. 98·89% and 1·11%.
20. (i) $^{198}_{79}Au \rightarrow {}^{198}_{78}Hg + {}^{0}_{-1}e(\beta^-)$
(ii) $N = (\frac{1}{2})^n N_0$; Here $N_0 = 1$ gm
$n = 4$ (number of lives)
or, $N = (\frac{1}{2})^4 \times 1 = \frac{1}{16}$.
21. Atomic weight = 206; Atomic number = 82.

22.
$$\begin{tikzcd} {}^{226}_{88}Ra \arrow[r, "-\alpha"] & {}^{222}_{86}Rn \arrow[r, "-\alpha"] & {}^{218}_{84}Po \arrow[r, "-\alpha"] & {}^{214}_{82}Pb \arrow[d, "-\beta"] \\ & & & {}^{214}_{83}Bi \end{tikzcd}$$

Mass no. = 222, 218, 214.
Atomic no. = 86, 84, 82, 83.
Group = zero, VI A, IV A, V A.

23. (iv).
24. (a) (iv).
25. (iii).
26. (iv).
27. (iii).
28. (i).
29. (iv).
30. (iv) least among four.
31. (i).
32. (i) and (iii).
33. (iv).
34. (i).
35. (iv).
36. (iv).
37. (iv).
38. (i).
39. (iii).
40. (ii).
41. (ii).
42. (iii).
43. (iv).
44. (ii).
45. (iii).
46. (iii).
47. (i).
48. (iii).
49. (i).
50. (iii).
51. (ii).
52. (iii).
53. (ii) and (iv).
54. (ii) and (iv).
55. (i).
56. (iv).
57. (iv).
58. (iv).
59. (iv).

CHAPTER 3. The Chemical Bonding (P. 162 – 168)

5. (i) Covalent; (ii) See valency, (iii) ionic, (iv) See valency.
22. (i) 6, (ii) 7, (iii) 6, (iv) 3.
23. (i) *sp*, (ii) sp^3, (iii) *sp*, (iv) sp^3, (v) sp^3,
25. (a) Nitrogen (N_2) and acetylene, (b) Cyanide (CN^-) and acetylene, (c) Phosphorus pentachloride and sulphur hexafluoride, (d) oxygen, (e) Aluminium chloride and borontrifluoride, (f) Ammonium chloride and sulphuric acid, (g) Hydrogen peroxide,

Sulphur dioxide, Sulphur trioxide, (h) Nitric oxide and Nitrogen dioxide, (i) Nitric oxide and Nitrogen dioxide.

28. (i) 4. (ii) 2. (iii) 6. (iv) 3.

29. **ionic** : (i), (v)
covalent : (ii), (iii), (iv), (vi).

32. **ionic** : (iv), (vi),
covalent : (i), (ii), (iii), (v).

33. **ionic** : (iv), (v), (ix), (x), (xi), (xii).
covalent : (i), (ii), (iii), (vi), (vii), (viii), (xiii), (xiv).

34. **ionic** : (i), (iv), (v).
covalent : (ii), (iii), (vi).

35. **ionic** : (b), (f).
covalent : (a), (e), (d), (e).

36. (i) 6; (ii) ionic, non.

(iii) covalent, coordinate; (iv) ionic, covalent, coordinate; (v) non, polar; (vi) electron; (viii) *sp* (ix) σ, π; (x) Hydrogen; (xi) lower.

37. 1 (c), 2 (e), 3 (b), 4 (a), 5 (d), 38. (i)—(xii), (ii)—(x),
(iii)—(vii), (iv)—(viii), (v)—(xi), (vi)—(ix).

40. 2. 41. 2. 42. 2. 43. 2. 44. 4. 45. 3.
46. 1. 47. 4. 48. 1. 49. 4. 50. 4. 51. 1.
52. 1. 53. 1. 54. 3. 55. 1. 56. 1. 57. 4.
58. 1. 59. 4. 60. CO_2. 61. H_2, but it is not compound.
62. $HCOOH$; CH_3COOH. 63. $X^+ + Y^-$. 64. 1.
65. 1. 66. 4. 67. 3. 68. 4. 69. 2. 70. 3.
71. 2.

CHAPTER. 4. **Periodic Classification** (Pages 123-128)

15. (i) CO_2, SO_2, NO_2, (ii) Br_2, Cl_2, F_2,
(iii) BaO, CaO, MgO, (iv) $Mg(OH)_2$, $NaOH$, KOH,
(v) CO_2, HCl, NH_3, (vi) Cl_2, F_2, Br_2,
(vii) *C*, *O*, *N*, (viii) *N*, *O*, *F*,
(ix) *Se*, *S*, *O*, (x) *Cu*, *Ag*, *Au*,
(xi) *Ag*, graphite, diamond, (xii) *Ca*, *Sr*, *Ba*,
(xiii) *I*, *Br*, *Cl*, (xiv) *Al*, *Mg*, *Na*.

28. (a) Mercury, (b) Bromine,
(c) Zinc and Aluminium, (d) Arsenic,
(e) Carbon, Phosphorus, Oxygen, Sulphur,
(f) White phosphorus, (g) Helium,
(h) chlorine.

29. (i) 8, (ii) Newland, (iii) d, (iv) Atomic number,
(v) decreases, increases.

30. *p*-block :—35,
d-block :—30.

32. (i)—(c); (ii)—(e); (iii)—(a); (iv)—(b); (v)—(d).
33. (1)—(e); (2)—(a): (3)—(d); (4)—(c); (5)—(b).
34. 1. (c), 2. (f), 3. (g), 4. (b), 5. (h),
6. CO_2 wrongly written CO, 7. (a), 8. (d).
35. 4, **36.** 2, **37.** 86 (wrongly written), actual *As*.
38. 4, **39.** 3, **40.** 2, **41.** 4, **42.** 1. **43.** 5,
44. 2, **45.** 2, **46.** 2, **47.** 1, **48.** 1, **49.** 4,
50. 1, **51.** 1, **52.** 2, **53.** 4, **54.** 2, **55.** 1,
56. 2, **57.** 3, **58.** 1.

CHAPTER 5. Hydrogen, Heavy hydrogen and Heavy water (181-183)

11. (a) ortho, (b) radioactive,
(c) isotope, (d) Deuterium,
(e) *Pd*, (f) one, one.
12. 1. (c), 2 (d), 3. (a), 4. (b).
13. **True**—(b), (c), (e), (f),
False—(a), (d), (g), (h).
14. 3, **15.** 2, **16.** 3, **17.** 1, **18.** 2, **19.** 3,
20. 2, **21.** 3, **22.** (written H^3) 2, **23.** 2, **24.** 1,
25. 1, **26.** 1, **27.** 3.

CHAPTER 6. Water and Hydrogen Peroxide (Pages 195-198)

25. 4, **26.** 1, **27.** 3, **28.** 4, **29.** 2, **30.** 3, **31.** 1,
32. 2, **33.** 4, **34.** 3, **35.** 3, **36.** 2.

CHAPTER 7. Study of Carbon Group of Elements (Pages 218-221)

18. (a) heavier, (b) neutral, acidic,
(c) bad, good, (d) CO_2, NO_2,
(e) 4, (f) sp^3, sp^2,
(g) 95%, (h) CO, N_2, (i) CO.
19. (i) b, (ii) d, (iii) a, (iv) c.
20. 4. **21.** 3, **22.** 2, **23.** 2, **24.** 1, **25.** 2,
26. 2, **27.** 2, **28.** 2, **29.** 4, **30.** 3, **31.** 2,
32. 2, **33.** 4.

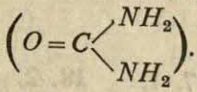
CHAPTER 8. Study of the Nitrogen Group of Elements (Pages 276-282)

31. (a) $8NH_3 + 3Cl_2 = N_2 + 6NH_4Cl$,
(b) $4Zn + 10HNO_3 = 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$,
(c) $2KI + 2HNO_2 = 2KOH + 2NO + I_2$,

(d) $6AgNO_3+PH_3+3H_2O=6Ag+6HNO_3+H_3PO_3$,
(e) $PCl_5+4H_2O=H_3PO_4+5HCl$,
(f) $6FeSO_4+4H_2SO_4+2KNO_3$
$=3Fe_2(SO_4)_3+4H_2O+K_2SO_4+2NO$,
(g) $Mg_3N_2+6H_2O=3Mg(OH)_2+2NH_3$.

33. (i) Alkaline pyragallol, (ii) Nessler's reagent, (iii) Ferrous sulphate and sulphuric acid, (iv) Carbon disulphide, (v) Ferrous sulphate, (vi) $FeSO_4$ and H_2SO_4, (vii) Ferrous sulphate.

40. (a) CaC_2, (b) fixation, Ammonia, (c) Mg_3N_2,
(d) allotropes, (e) white, (f) red,
(g) insoluble.

47. (a) N_2O (Nitrous oxide), (b) Ammonia (NH_3)
(c) Carbon monoxide (CO), Nitric oxide (NO),
(d) Nitrous acid (HNO_2) and Hydrogen peroxide (H_2O_2),
(e) Ammonium nitrate (N_2O), (g) Phosphine (PH_3),
(h) Hydrazoic acid (N_3H), (i) Nitric acid (HNO_3),
(j) Urea 
$\left(O=C\begin{matrix}NH_2\\NH_2\end{matrix}\right)$.

48. 1 (c), 2 (d), 3 (a), 4 (f), 5 (b), 6 (e).
49. **True**—(e), (f), (g), (h), (i), (j), (l).
False : (a), (b), (c), (d), (k).
50. 4. 51. 4. 52. 4. 53. 4. 54. 3. 55. 2.
56. 4. 57. 2. 58. 3. 59. 4. 60. 1. 61. 2.
62. 4. 63. 3. 64. 4. 65. 5. 66. 3. 67. 4.
68. 4. 69. 1. 70. 3.

Chapter 9. Study of the Oxygen Group of Elements (Pages 327-330)

17. $A=Cu$, $B=CuSO_4$, $C=SO_2$, $D=CuS$, $E=[Cu(NH_3)_4]SO_4$, $F=$ Sulphur. For reactions see previous pages.
18. $A=FeS$; $B=H_2S$; $C=FeCl_2$; $D=PbS$; $E=AgCl$; $F=[Ag(NH_3)_2]Cl$.
24. 1. 25. 4. 26. 2. 27. 3 ($N_2Cr_2O_7\rightarrow K_2Cr_2O_7$).
28. 3. 29. 4. 30. 2. 31. 2. 32. 4. 33. 3.
34. 3. 35. 4. 36. 2. 37. 3. 38. 3. 39. 4.
40. 4. 41 2. 42. 4.

Chapter 10. Study of the Elements of Halogen Family (Pages 370-374)

25. (i) HOI, $HOBr$, $HOCl$, (ii) HCl, HBr, HI,
(iii) I_2, Br_2, Cl_2, (iv) arranged,
(v) I_2, Br_2, Cl_2, F_2, (vi) I_2, Br_2, F_2, Cl_2,

(vii) I_2, Br_2, Cl_2, F_2, (viii) I_2, Br_2, Cl_2, F_2,
(ix) I_2, Br_2, Cl_2, F_2, (x) F_2, Cl_2, Br_2, I_2,
(xi) I_2, Br_2, Cl_2, F_2, (xii) F_2, Cl_2, Br_2, I_2,
(xiii) F_2, Cl_2, Br_2, I_2, (xiv) F_2, Cl_2, Br_2, I_2,
(xv) F_2, Cl_2, Br_2, I_2.

26. See the chapters.

27. (A) (i) KCl, $KClO$, (ii) Hydrogen chloride, (iii) $NaIO_3$.
(B) (i) 5 moles, (ii) Fused $NaCl$, (iii) Hypo,
(iv) Oxidation, Permanent.

28. 1 (c), 2 (d), 3 (e), 4 (b), 5 (a).

29. (i) $X = Cl_2$, $Y = NaCl$, $Z = [Ag(NH_3)_2]Cl$,
(ii) $A = NaCl$, $B = HCl$, $C = AgCl$, $D = Cl_2$.

30. 2. **31.** 3. **32.** 3. **33.** 2. **34.** 2. **35.** 1.
36. 1. **37.** 4. **38.** 2. **39.** 2. **40.** 3. **41.** 1.
42. 4. **43.** 2. **44.** 4.

CHAPTER 11. Metals And General Metallurgical Operations (Pages 388-389)

11. (i) (c), (ii) (c), (iii) (a), (iv) (b).
13. 3. **14.** 4. **15.** 3. **16.** 4. **17.** 3. **18.** 4.
19. 5, **20.** 4. **21.** 5.

CHAPTER 12. Compounds of Metals (Page 396)

6. (a) amphoteric, (b) insoluble.
(c) soluble, (d) CuO is missing,
(e) KNO_2, (f) soluble.

7. 1. **8.** 2. **9.** 2. **10.** 2. **11.** 3. **12.** 4.

CHAPTER 13. Study of Sodium (Pages 425-429)

14. (a) $Na_2S_2O_3.5H_2O$, (b) $Na_2CO_3.10H_2O$,
(c) $NaOH$, (d) $NaHCO_3$,
(e) $Na_2B_4O_7.10H_2O$, (f) KNO_3,
(g) $NaNO_3$, (h) $Na_2SO_4.10H_2O$,
(i) Na_2SiO_3, (j) $K_2SO_4\ Al_2(SO_4)_3.24H_2O$.

15. Hint (a) Ring test→KNO_3,
(b) $K_2Cr_2O_7$ paper turns green→Na_2SO_3,
(c) Ring test→$NaNO_3$,
(d) Flame test→$NaCl$ (Golden yellow flame),
(e) $BaCl_2$ sol^n test→Na_2SO_4,
(f) Golden yellow colour flame ($NaCl$).

21. (a) $Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$,
(b) $2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$,
(c) $P_4 + 3NaOH + 3H_2O = PH_3 + 3NaH_2PO_2$,

(d) $2NaOH+CO_2 \rightarrow Na_2CO_3+H_2O$,
(e) $ZnSO_4+4NaOH \rightarrow Na_2SO_4+Na_2ZnO_2+2H_2O$.

23. 1 (d), 2 (h), 3 (g), 4 (a), 5 (f), 6 (b), 7 (c), 8 (e).
24. 1 (b), 2 (b), 3 (a), 4 (c).
26. **Hint.** (a) Golden yellow flame→$NaNO_2$, (b) same as (b), (c) Ring test for nitrate, (d) same as (a), (e) salt+dil. HCl→gas, which turns dichromate paper green, (f) with $BaCl_2$ solution, Na_2SO_4 solution gives white precipitate.

28. (i) $A \rightarrow Na,\ B=Cl_2,\ C=NaOH,\ D=Na_2CO_3$
(ii) $A=Na_2CO_3,\ B=NaHCO_3,\ C=Na_2CO_3,\ D=CO_2$.

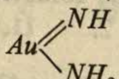
29. (3). **30.** (3). **31.** (4). **32.** (1). **33.** (2).
34. (4). **35.** (4). **36.** (4). **37.** (2). **38.** (2).
39. (2). **40.** (4). **41.** (4). **42.** (3). **43.** (3).
44. (2). **45.** (2).

CHAPTER 14. Study of Group I-B of Elements

(Pages 465-467)

20. (i) $AgCl+2KCN=K[Ag(CN)_2]+KCl$
(ii) $AgCl+2Na_2S_2O_3=Na_3[Ag(S_2O_3)_2]+NaCl$,
(iii) $2CuSO_4+10KCN=2K_3[Cu(CN)_4]+2CuCN+C_2N_2+2K_2SO_4$,
(iv) $CuSO_4+4NH_4OH=[Cu(NH_3)_4]SO_4+4H_2O$,
(v) $2AuCl_3+3SnCl_2=2Au+3SnCl_4$.

21. 1. (f), 2. (e), 3. (b), 4. (a), 5. (g), 7. (d).

6. It should be  then answer is (c).

$Au(=NH)(NH_2)$

22. (a) acidic, (b) Horn silver,
(c) It should be $Ag_2S.Sb_2S_3$ then ruby silver, (d) Red.

23. 3. **24.** 4. **25.** 1. **26.** 3. **27.** 2. **28.** 3.
29. 2. **30.** 2. **31.** 3. **32.** 1.

CHAPTER 15. Study of Group II-A Elements in Periodic Table

(Pages 488-491)

11. 1 (c), 2 (h), 3 (a), 4 (b), 5 (d), 6 (e), 7 (f), 8 (g),
13. (i) $CaSO_4.\frac{1}{2}H_2O$, (ii) desiccating,
(iii) purgative, (iv) acetylene,
(v) Fertiliser, (vi) S, (vii) 4th, II.

15. (2). **16.** (3). **17.** (1). **18.** (3). **19.** (3).
20. (1). **21.** (2). **22.** (2). **23.** (3). **24.** (3).

25. (1). **26.** (2). **27.** (3). **28.** (3). **29.** (1).
30. (2). **31.** (2). **32.** (3).

CHAPTER 16. Study of Group II-B of Elements
(Pages 518-521)

7. (a) $3HgS+12HCl+2HNO_3=3H_2HgCl_4+2NO+3S+4H_2O$,
(b) $4Zn+NaNO_3+7NaOH=4Na_2ZnO_2+NH_3+2H_2O$,
(c) $4Zn+10HNO_3=4Zn(NO_3)_2+N_2O+5H_2O$,
(d) $Zn+2NaOH=Na_2ZnO_2+H_2$,
(e) $2HgCl_2+SnCl_2=Hg_2Cl_2+SnCl_4$
(f) $HgCl_2+4KI=K_2[HgI_4]$,
(g) $HgCl_2+H_2S=HgS+2HCl$,
(h) $2ZnSO_4+K_4[Fe(CN)_6]=Zn_2[Fe(CN)_6]+K_2SO_4$.

12. (a) IIB, (b) liquid, (c) $ZnSO_4.7H_2O$,
(d) NH_3, (e) ZnO, (f) Amalgam.

13. (i) $ZnCO_3$, (ii) Hg_2Cl_2, (iii) ZnO,
(iv) $ZnSO_4.7H_2O$, (v) $K_2[HgI_4]+KOH$, (vi) HgS,
(vii) ZnO, (viii) $ZnO.CoO$. (ix) $HgCl_2$ (x) HgS.
(xi) $BaSO_4+ZnS$, (xii) ZnS, (xiii) Zn_2SiO_4.

17. Hint. (a) By H_2S. (b) Dil. HCl and H_2S.
(c) Dil. HCl and H_2S.

18. 2. **19.** 3. **20.** 1. **21.** 1. **22.** 1. **23.** 4.
24. 1. **25.** 1. **26.** 1. **27.** 2. **28.** 2. **29.** 2.
30. 1. **31.** 3. **32.** 2. **33.** 2. **34.** 2. **35.** 1.
36. 1. **37.** 3. **38.** 4. **39.** 3.

CHAPTER 17. Aluminium (Pages 532-533)

3. (a) $Al_4C_3+12H_2O\rightarrow 4Al(OH)_3+3CH_4$,
(b) $2Al+2NaOH+2H_2O\rightarrow 2NaAlO_2+3H_2$,
(c) $AlN+3H_2O\rightarrow Al(OH)_3+NH_3$,
(d) $Al_2O_3+3C+N_2\rightarrow 2AlN+3CO$,
(e) $AlCl_3+4NaOH\rightarrow NaAlO_2+3NaCl+2H_2O$,
(f) $Al_2O_3+3C+3Cl_2\rightarrow 2AlCl_3+3CO$.

8. (a) mineral, (b) $Al_2O_3\,2H_2O$, (c) eight,
(d) active, (e) alloy, Al, Mg.

15. 2. **16.** 1. **17.** 3. **18.** 1. **19.** 4. **20.** 3.

CHAPTER 18. TIN AND LEAD
(Pages 548-551)

7. True : (i), (ii), (v), (vi).
False : (iii), (iv).

9. Hint. (a) $HgCl_2$ solution, (b) $HgCl_2$ solution,
(c) Ring test for nitrate, wrongly written $PbCl_3$, should be $PbCl_2$.

12. (a) Tin stone, (b) Lead, (c) reducing,
(d) covalent, (e) paint, (f) anti-knock.

13. (i)—(d), (ii)—(f), (iii)—(b), (iv)—(a), (v)—(h)
wrongly written C_1. (vi)—(c), (vii)—(e), (viii)—(g).

14. 3. **15.** 3. **16.** 4. **17.** 1. **18.** 3. **19.** 5.
20. 3. **21.** 3. **22.** 2. **23.** 5. **24.** 1. **25.** 3.
26. 5. **27.** 1.

CHAPTER 19. IRON

(Pages 565-567)

11. (i) acidic, (ii) acidic, (iii) iron, (iv) Jeweller,
(v) Fe_3O_4.

14. (i) $FeSO_4.7H_2O$, (ii) $FeSO_4.(NH_4)_2SO_4.6H_2O$,
(iii) Fe_3O_4, (iv) $K_2SO_4.Fe_2(SO_4)_3.24H_2O$,
(v) FeS_2, (vi) Fe_2O_3, (vii) $FeCl_3$ or Fe_2Cl_6.

15. (a) $Fe_3O_4+CO\rightarrow 3FeO+CO_2$,
(b) $2FeSO_4\rightarrow Fe_2O_3+SO_2+SO_3$,
(c) $4FeS_2+11O_2\rightarrow 2Fe_2O_3+8SO_2$,
(d) $3Fe^{++}+NO_3^{-1}+4H^+\rightarrow 3Fe^{+3}+NO+2H_2O$,
(e) $5Fe^{++}+8H^++MnO_4^{-1}\rightarrow 5Fe^{+3}+5H_2O+Mn^{+2}$,
(wrongly written as Cr^{3+}, should be Mn^{+2})
(f) $2FeCl_3+H_2S\rightarrow 2FeCl_2+2HCl+S$,
(g) $2FeCl_3+SnCl_2\rightarrow SnCl_4+2FeCl_2$,
(h) $4FeCl_3+3K_4[Fe(CN)_6]\rightarrow 12KCl+Fe_4[Fe(CN)_6]_3$,
(i) $FeCl_3+3NH_4CNS\rightarrow NH_4Cl+Fe(CNS)_3$,
(j) $Fe_2(SO_4)_3\rightarrow Fe_2O_3+3SO_3$,
(k) $6FeSO_4+3H_2SO_4+2HNO_3\rightarrow 3Fe_2(SO_4)_3+2NO+4H_2O$.

16. 3. **17.** 1. **18.** 3. **19.** 3. **20.** 4. **21.** 3.
22. 3. **23.** 4. **24.** 3. **25.** 2. **26.** 2. **27.** 4.
28. 1. **29.** 3. **30.** 4. **31.** 2. **32.** 3.

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